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THE WOLFF REARRANGEMENT OF DIAZOKETONES

by



EDWARD JOSEPH PIOTRKOWSKI

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

SPRING, 1973

75-89

THE UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled "THE WOLFF REARRANGEMENT OF DIAZOKETONES" submitted by EDWARD JOSEPH PIOTRKOWSKI in partial fulfilment of the requirements for the degree of Master of Science.

ABSTRACT

The photochemical and thermal WR of 2-diazo-1-propionaldehyde and α -diazoacetone, ^{13}C , labelled in the carbonyl position, was investigated. The gas phase photolyses yielded mainly N_2 , CO , C_2H_4 and C_2H_2 . Mass spectral analyses of the CO fractions indicated $\sim 20\%$ scrambling in both cases, thus supporting earlier evidence for the intermediacy of oxirenes in the photochemical WR of α -diazo-ketones. Liquid phase photolyses in methanol yielded labelled esters which were shown by n.m.r. to be only ca. 6% scrambled in the CO position. Some scrambling was also detected in the thermolysis experiments. Since the gas phase photochemical WR of both asymmetrically substituted diazoketones yielded the same amount of scrambling it was concluded that the controlling step in the isotopic scrambling reaction cannot be the ring opening of the oxirene structure. The gas phase photolysis of methylketene- ^{13}CO yielded 16% scrambling, only slightly less than that from the parent diazoketones.

The photolysis of α -diazoacetophenone in cyclohexene yielded dilactone, which presumably arises from a ketene-ketocarbene addition reaction; in methanol and iso-propanol the major products are esters. Triplet photosensitization yielded mainly acetophenone, formed via H-

abstraction by the triplet ketocarbene from the solvent. These results conclusively prove that the reactive intermediate in the photochemical WR of α -diazoketones is a singlet.

It is likely that oxirene formation is a relatively minor process in the photolysis of diazopropanones.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the guidance and assistance provided by Professor O. P. Strausz.

Special thanks are due to Dr. E. M. Lown for help in the preparation of this thesis.

It has been a pleasure to be associated with the members of the Photochemistry Laboratory, and the author is grateful for the many fruitful discussions and ideas presented during the course of this work. The assistance of the technical staff of this group was particularly valuable.

The author wishes also to thank the members of I.R. and N.M.R. Laboratories of the Chemistry Department for their co-operation and assistance.

TABLE OF CONTENTS

	Page
ABSTRACT	iii
ACKNOWLEDGEMENTS	v
LIST OF TABLES	ix
LIST OF FIGURES	xi
CHAPTER 1 INTRODUCTION	1
1.1 History and Review	1
1.2 Aim of the Present Work	17
CHAPTER 2 EXPERIMENTAL	21
2.1 Apparatus and Instrumentation	21
2.2 Materials	27
2.2.1 Preparation of 1,1-Diethoxypropane- 1- ¹³ C, II	27
2.2.2 Preparation of 2-methyl-3-dimethyl- aminoacrolein- ¹³ CO, III	27
2.2.3 Preparation of 2-diazopropion- aldehyde- ¹³ CO, I.	29
2.2.4 Preparation of α-diazoacetone- ¹³ CO, IV	30
2.2.5 Preparation of methylketene- ¹³ CO, V .	31
2.2.6 Preparation of α-diazoacetophenone, VI	32
2.2.7 Preparation of 7-Norcaryl-phenyl ketone, VII	32

Table of Contents cont'd.

	Page
2.2.8 Preparation of bicyclohexenyl, VIII .	33
2.3 Methods	34
2.3.1 Photolyses	34
2.3.2 Thermolyses	36
2.3.3 The direct and sensitized photolysis of α -diazacetophenone, VI	37
CHAPTER 3 RESULTS	39
3.1 2-Diazopropionaldehyde- ^{13}CO	39
3.1.1 Photolysis in the gas phase	39
3.1.2 Photolysis in methanol solution	42
3.1.3 Thermolysis	45
3.2 α -Diazacetone- ^{13}CO	45
3.2.1 Photolysis in the gas phase	45
3.2.2 Photolysis in methanol solution	47
3.2.3 Thermolysis	49
3.3 Methylketene	51
3.4 α -Diazacetophenone	52
3.4.1 Polar Solvents	53
3.4.2 Non-polar solvents	56
CHAPTER 4 DISCUSSION	60
CHAPTER 5 SUMMARY AND CONCLUSIONS	75

Table of Contents cont'd.

	Page
BIBLIOGRAPHY	78

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Extent of Oxirene Participation in the WR of Diazoketones.	10
2	Product Yields from the Gas Phase Photo- lysis of I	40
3	Product Yields from the Liquid Phase Photo- lysis of I	44
4	Mass Spectrometric Analysis of the Noncon- densable Fraction from Gas Phase Photolysis of IV	47
5	Product Yields from the Gas Phase Photoly- sis of IV	48
6	Product Yields from the Liquid Phase Photo- lysis of IV	51
7	Product Yields from the Gas Phase Photoly- sis of V	53
8	Product Yields from the Direct Photolysis of VI in Polar Solvents	54
9	Product Yields from the Sensitized Photolysis of VI in Polar Solvents	55
10	Ester to Acetophenone Product Ratios . . .	55
11	Product Yields from the Direct and Photo- sensitized Photolysis of VI in Cyclohexene	57

List of Tables cont'd.

<u>Table</u>		Page
12	Summary of Experimental Results	61
13	Direct and Sensitized Photolysis of α - Diazoacetophenone	69

LIST OF FIGURES

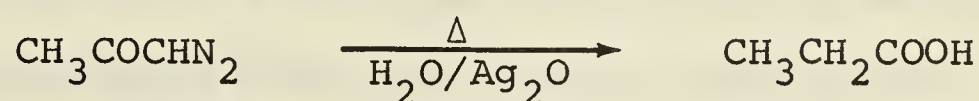
<u>Figure</u>		<u>Page</u>
1	a) Immersion well; b) reaction vessel; c) photolysis assembly	22
2	a) High resolution mass spectrum of the noncondensable fraction from the photolysis of 2-diazopropionaldehyde- ^{13}CO ; b) high resolution background	41
3	a) Nuclear magnetic resonance spectrum of labelled methyl propionate from the photo- lysis of 2-diazopropionaldehyde- ^{13}CO in methanol; b) expanded n.m.r. spectrum of methylene portion of the methyl propionate; c) expanded n.m.r. spectrum of methoxy portion of the methyl propionate	43
4	a) High resolution mass spectrum of the noncondensable fraction from the photolysis of α -diazoacetone- ^{13}CO ; b) high resolution background	46
5	a) Nuclear magnetic resonance spectrum of labelled methyl propionate from the photo- lysis of α -diazoacetone- ^{13}CO in methanol; b) expanded n.m.r. spectrum of methylene portion of the methyl propionate; c) ex-	

List of Figures cont'd.

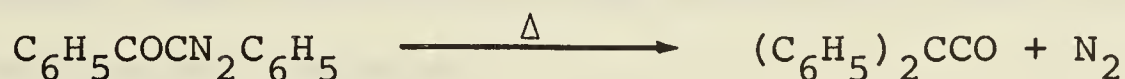
Figure		Page
	panded n.m.r. spectrum of methoxy portion of the methyl propionate	50
6	Calculated enthalpy changes for the decom- position of 2-diazopropionaldehyde and α -diazoacetone	66

CHAPTER 1INTRODUCTION1.1 History and Review

In 1902 Wolff^{1,2} treated α -diazo-2-propanone with hydroxide ion and discovered that, instead of the usual substitution, a rearrangement had taken place:



Independently, Schroeter^{3,4} discovered a similar rearrangement in the thermolysis of azibenzil:

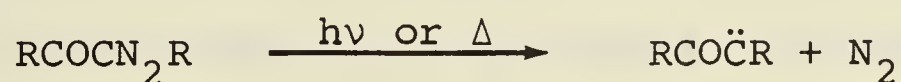


Subsequent work showed that all α -diazoketones can be converted into various rearrangement products such as ketenes, acids or esters depending upon the solvent and phase and that these conversions can be brought about catalytically, photochemically or thermally. These transformation reactions of α -diazoketones, called the Wolff rearrangement (WR), have been widely exploited in synthetic organic chemistry but their mechanistic aspects have only been vaguely explored until recently.

There have been several mechanisms proposed in

the literature for the WR sequence. All consider the migration of the R group to be an intramolecular process not involving ionic or free radical intermediates since the stereochemical information content of the R group is retained upon conversion.⁵

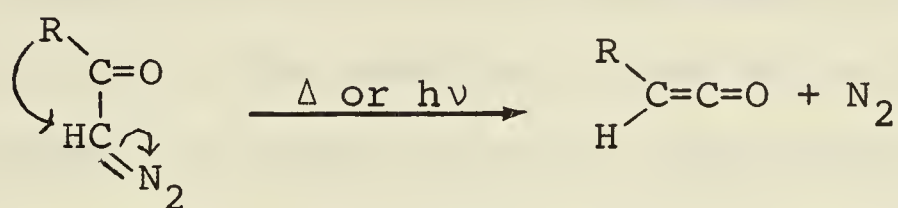
The pathway originally proposed by Wolff,^{1,2} was generally accepted for many years in spite of the fact that the WR is so rapid that repeated attempts to trap ketocarbenes have been mostly unsuccessful. Wolff proposed that the first stage of the rearrangement is detachment of nitrogen from the diazoketone to form a ketocarbene intermediate which then rearranges to ketene. The ketene then reacts with the solvent to give an acid or a derivative thereof:



$\text{R}' = \text{OH}, \text{OAc}, \text{NH}_2, \text{etc.}$

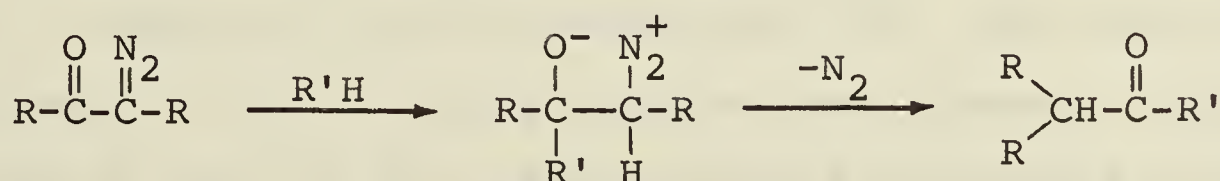
There is some evidence for the intermediacy of ketocarbenes however. For example, small yields of oxazole derivatives, the 1,3-addition products of ketocarbenes,

On the basis of nmr studies of hindered rotation about the C-C bond in diazoketones, Kaplan and Meloy^{16,17} suggested that the WR is a one-step concerted rearrangement with simultaneous extrusion of nitrogen:



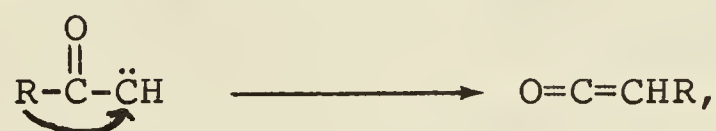
It was found that the preferred conformation is cis, i.e. in which the diazo and carbonyl groups are in a cis relationship and the R group is trans to the leaving group. Diazoketones in this conformation would readily undergo the WR whereas those in the trans configuration preferentially isomerize to an α,β -unsaturated ketone.¹⁸ Kinetic studies do not support a concerted mechanism for the WR however¹⁹⁻²¹ and theoretical calculations²² predict a prohibitively high activation energy, ca 114 kcal/mole, for such a process.

Yet another alternative pathway, first proposed by Eistert²³ and discussed recently by Wilds et al.,²⁴ involves an initial protonation step to form a betaine which then rearranges:

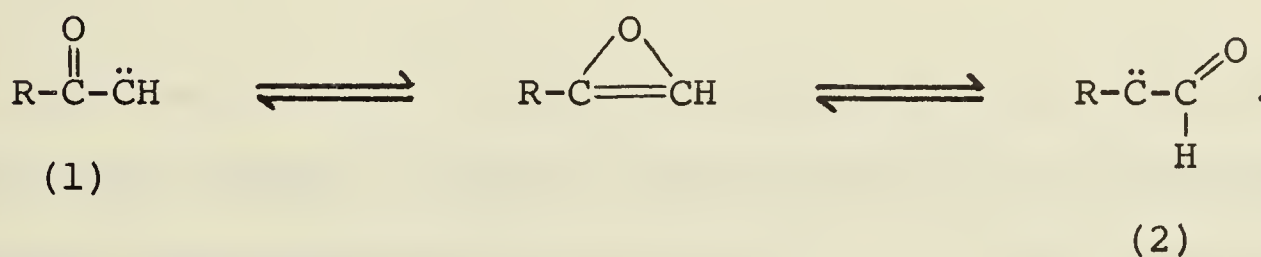


However, Bartz and Regitz²⁵ investigated the thermal WR in nucleophilic solvent such as alcohols and amines and concluded that the kinetics of nitrogen evolution were not compatible with a protonation step.

Returning now to the ketocarbene-ketene mechanism proposed by Wolff, the question arises as to the mechanism by which ketene is formed from the ketocarbene: does it form via a simple intramolecular migration of the R group,

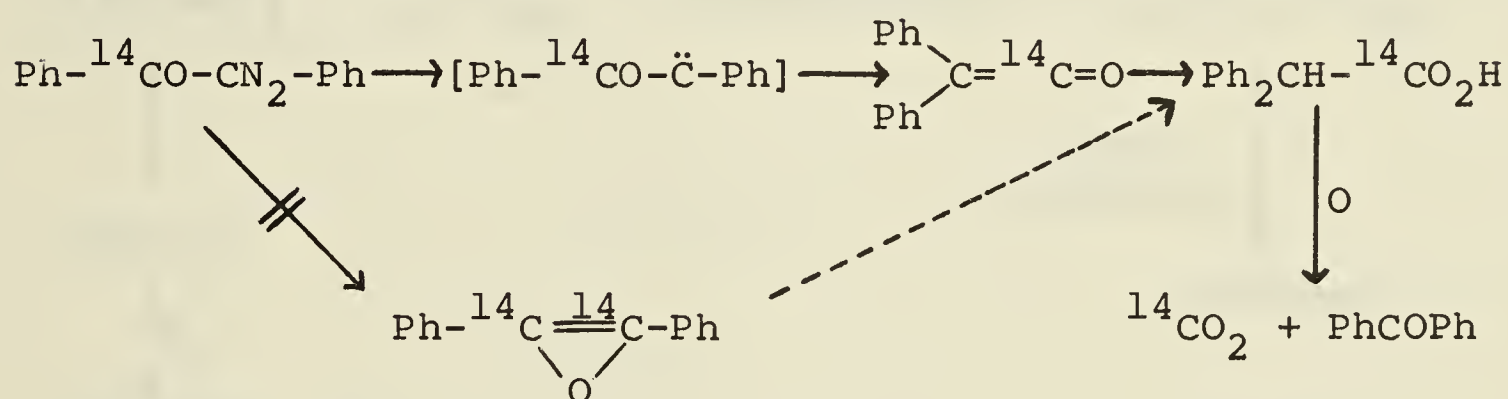


or is an oxirene structure involved in the sequence, e.g.



Direct proof of the intermediacy of oxirene could be obtained by ¹³C labelling in the carbonyl position since the resulting ketene (or its secondary decomposition products) would be isotopically "scrambled" if an equilibrium exists between ketocarbenes (1) and (2) via the oxirene structure. Nearly thirty years ago Huggett²⁶ found that no scrambling took place in the WR of diazoacetophenone-¹³CO; the degree of enrichment in the starting material was, however, quite low and in view of the unsophisticated techniques of the

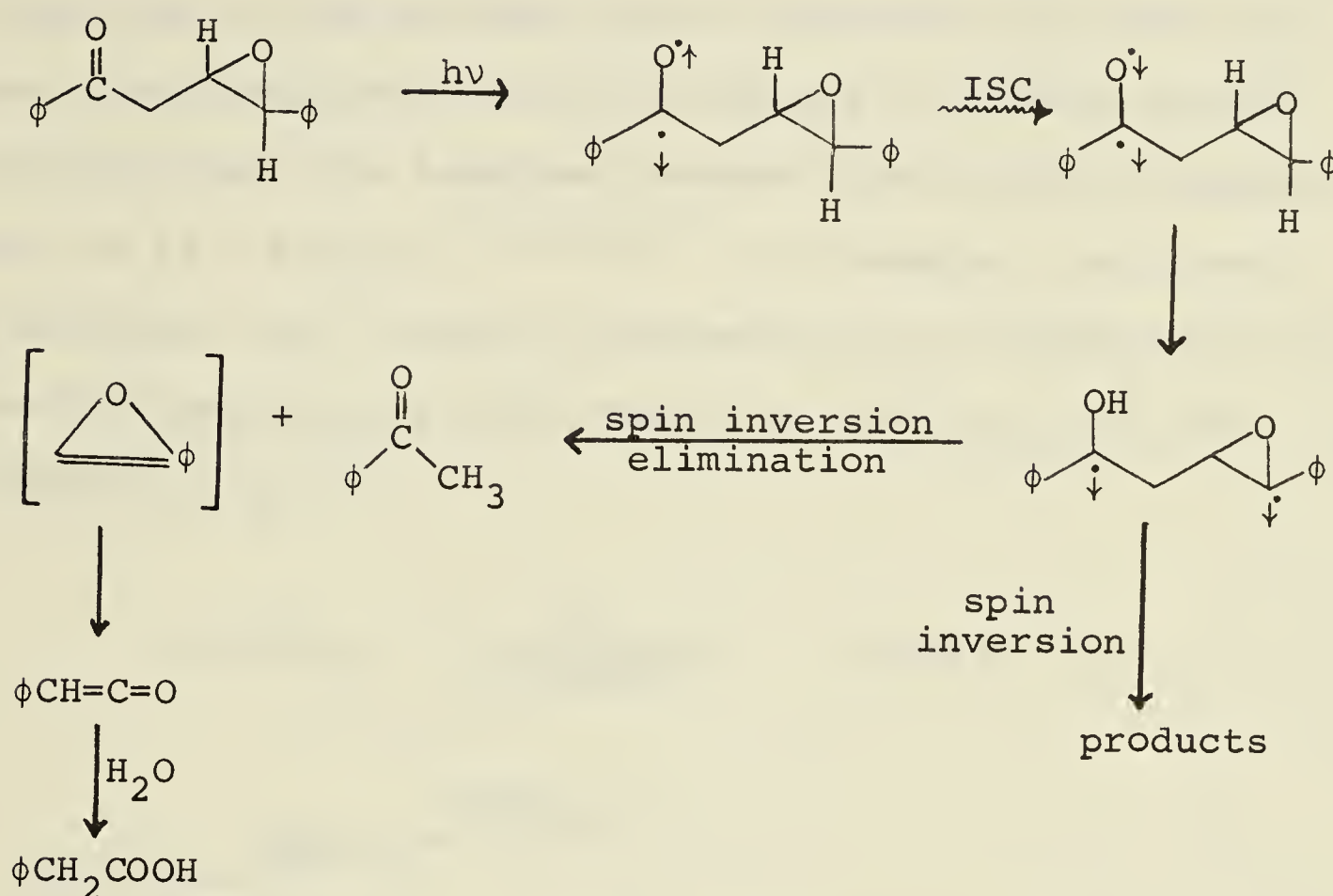
time, the results should be viewed with caution. Franzen²⁷ later found that no scrambling occurred in the thermal and photochemical WR of azibenzil-¹⁴C and concluded that oxirene is not an intermediate. Diphenyl ketene, formed by rearrangement of the intermediate ketocarbene, reacted with water to form diphenylacetic acid in which the entire amount of labelling was retained in the carbonyl group:



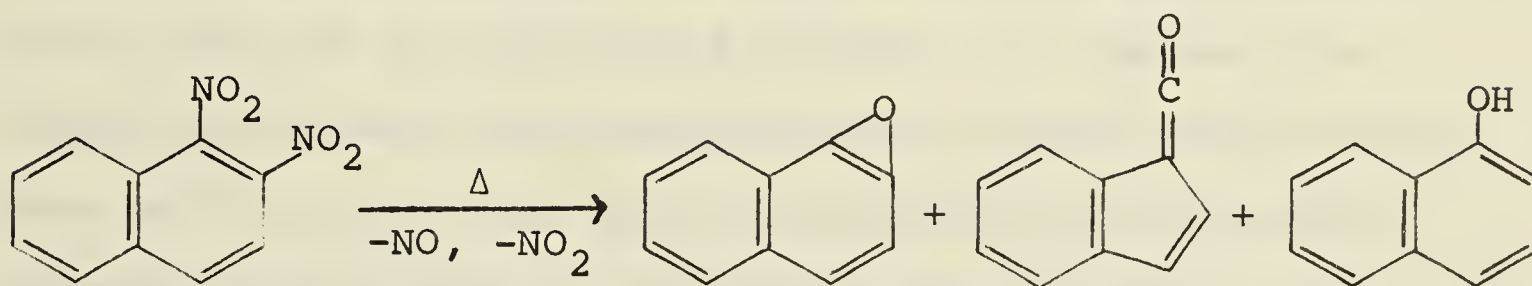
The position of the ¹⁴C atom in diphenylacetic acid was determined through oxidative decarboxylation and measurements of the radioactivity of the CO₂. On the basis of Franzen's results it was believed that oxirene is not an intermediate of the WR. It should be mentioned at this point that oxirene or its derivatives have never been isolated. They have been proposed as intermediates in some reactions such as the peroxidation of acetylenes,²⁸⁻³²



the photolysis of trans-1,4-diphenyl-3,4-epoxy-1-butanone,³³



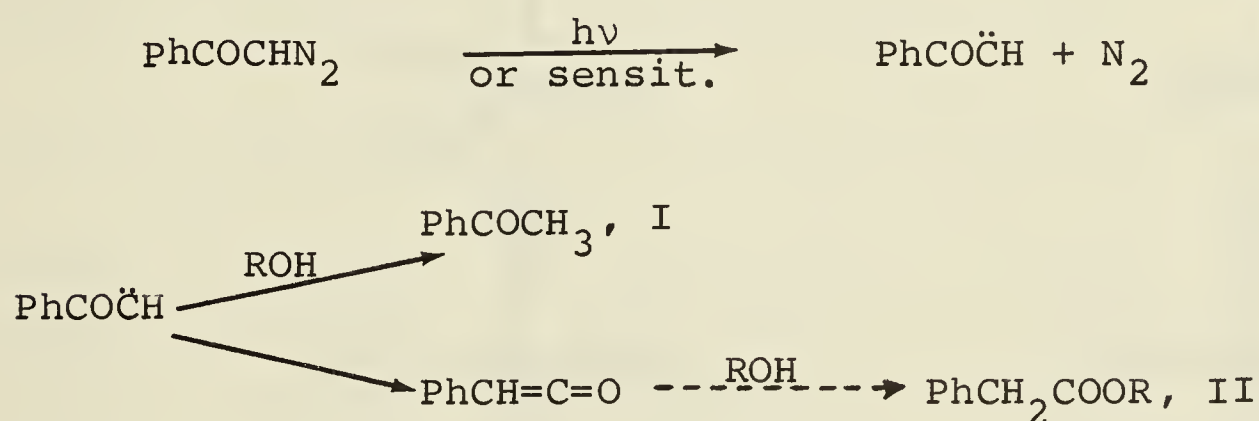
and in the pyrolytic mass spectrometric decomposition of 1,2-dinitronaphthalene,³⁴



but the mechanisms proposed are mainly speculative.

The photochemical WR is an important synthetic process and offers the distinct advantage that it can be brought about under mild experimental conditions. In

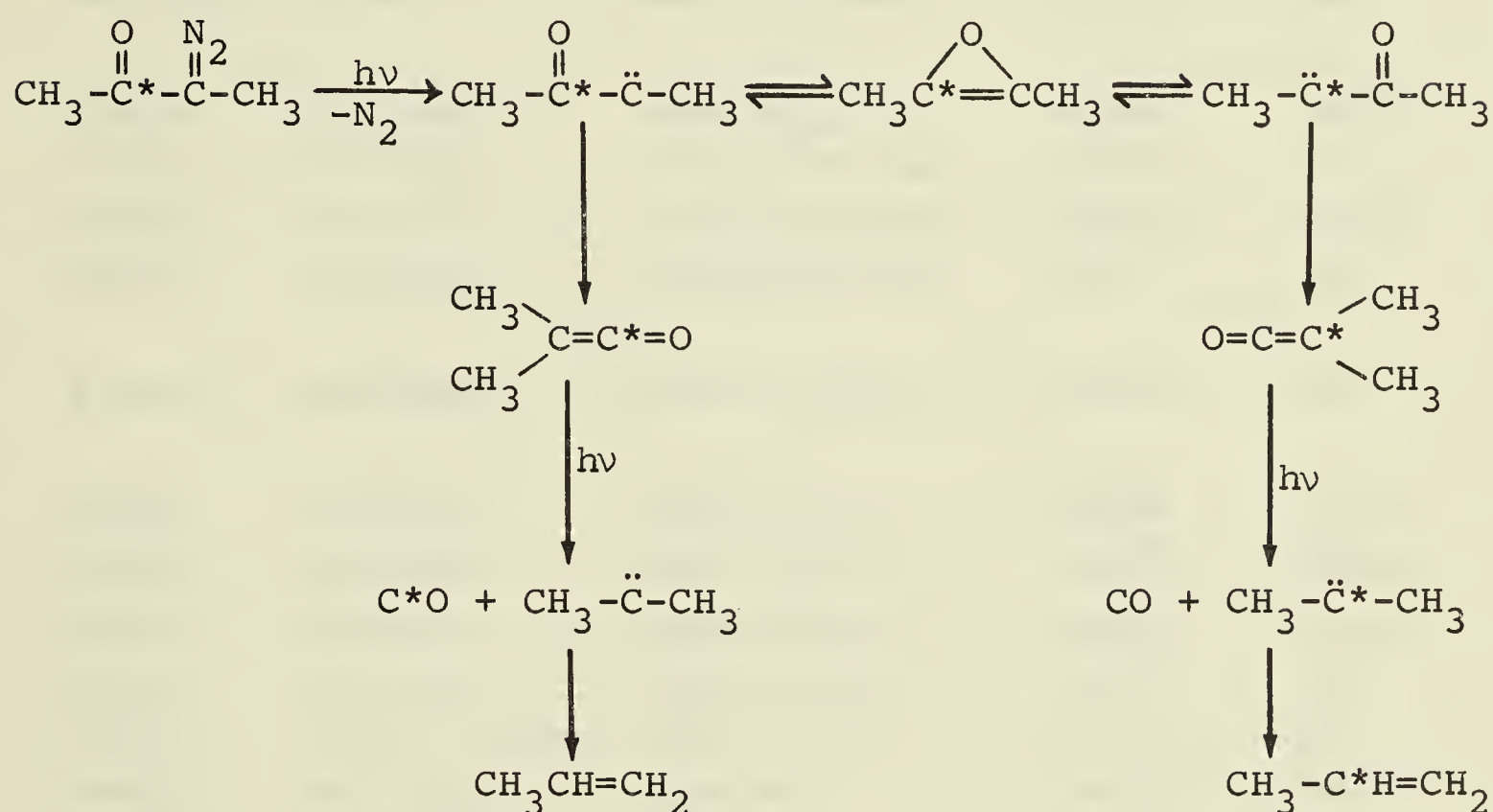
addition to the mechanistic problems outlined above, the character of the excited states responsible for the various transformations has to be defined. There is strong evidence that the reactive intermediate in the photochemical WR is a singlet.^{9,10,35,36} For example, the direct photolysis and (triplet) photosensitized decomposition of α -diazacetophenone were studied by Padwa et al.⁹ and Hammond et al.¹⁰:



In alcoholic solution the direct photolysis resulted in high yields of the rearranged product, II, whereas the triplet photosensitized decomposition yielded mainly acetophenone.⁹ On the other hand, the product distributions from the two reactions were identical in olefinic solvents¹⁰ and it was claimed that there is a rapid intersystem crossing in one of the intermediates.

The gas phase photochemical WR of 3-diazo-2-butanone, 3-diazo-2-propanone, ethyl and methyl diazoacetate and azibenzil was recently examined by Strausz et

al.³⁷⁻³⁹ using carbon-13 labelling in the carbonyl positions and from the observed scrambling in the products it was concluded that oxirene is an important intermediate in the reaction. A typical reaction scheme is outlined below.



Subsequently, the investigation was broadened to examine the effects of substituents, phase, solvent, and wavelength of excitation.⁴⁰ The results are shown in Table 1, and can be summarized as follows:

- 1) the extent of scrambling, indicative of oxirene participation, is highest in the case of the gas phase photolysis of symmetrical diazoketones;
- 2) upon going to the condensed phase, the oxirene

Table 1

Extent of Oxirene Participation in the WR of Diazoketones.

Compound	Reaction	Phase	Conditions	% Yield of Oxirene
$\text{CH}_3\text{COCN}_2\text{CH}_3$	photolysis	gas ~5 torr	$\lambda > 2200\text{\AA}$	100
$\text{CH}_3\text{COCN}_2\text{CH}_3$	photolysis	cyclo- C_5H_{10} solution	$\lambda > 2200\text{\AA}$	~70
$\text{CH}_3\text{COCN}_2\text{CH}_3$	photolysis	dioxane-water sol.	$\lambda > 2200\text{\AA}$	~61
$(\text{CH}_3)_2\text{C}=\text{C}=\text{O}$	photolysis	gas	$\lambda > 2200\text{\AA}$	~20
$(\text{CH}_3)_2\text{C}=\text{C}=\text{O}$	photolysis	cyclo- C_5H_{10} sol.	$\lambda > 2200\text{\AA}$	~16
$\phi\text{COCN}_2\phi$	photolysis	cyclo- C_5H_{10} sol.	$\lambda > 2000\text{\AA}$	60-70
$\phi\text{COCN}_2\phi$	photolysis	dioxane-water sol.	$\lambda > 2200\text{\AA}$	~50
$\phi\text{COCN}_2\phi$	photolysis	dioxane-water sol.	$\lambda > 2800\text{\AA}$	~30-35
$\phi\text{COCN}_2\phi$	thermolysis	dioxane-water sol.	100°C	nil
$\phi_2\text{C}=\text{C}=\text{O}$	photolysis	cyclo- C_5H_{10} sol.	$\lambda > 2000\text{\AA}$	30
$\phi\text{COCN}_2\text{H}$	photolysis	cyclo- C_5H_{10} sol.	$\lambda > 2000\text{\AA}$	12-21
$\phi\text{COCN}_2\text{H}$	photolysis	cyclo- C_5H_{10} sol.	$\lambda > 2200\text{\AA}$	20-23
$\phi\text{COCN}_2\text{H}$	photolysis	cyclo- C_5H_{10} sol.	$\lambda > 2800\text{\AA}$	27-29
$\phi\text{COCN}_2\text{H}$	photolysis	cyclo- C_5H_{10} sol.	$\lambda > 3600\text{\AA}$	~53
$\phi\text{COCN}_2\text{H}$	Michler's ketone	cyclo- C_5H_{10} sol.	sensitized	~57
$\phi\text{COCN}_2\text{H}$	photolysis	CH_3OH sol.	$\lambda > 2000\text{\AA}$	19
$\phi\text{COCN}_2\text{H}$	photolysis	CH_3OH sol.	$\lambda > 2200\text{\AA}$	15
$\phi\text{COCN}_2\text{H}$	photolysis	CH_3OH sol.	$\lambda > 2800\text{\AA}$	8
$\phi\text{COCN}_2\text{H}$	Michler's ketone	CH_3OH sol.	sensitized	12
$\phi\text{HC}=\text{C}=\text{O}$	photolysis	cyclo- C_5H_{10} sol.	$> 2220\text{\AA}$	~4
$\text{CH}_3\text{COCN}_2\text{H}$	photolysis	gas ~10 torr	$\lambda > 2200\text{\AA}$	>27
$\text{C}_2\text{H}_5\text{OCOCN}_2\text{H}$	photolysis	gas ~5 torr	$\lambda > 2200\text{\AA}$	>32
$\text{C}_2\text{H}_5\text{OCOCN}_2\text{H}$	thermolysis	cyclo- C_5H_{10} sol.	100°	nil
$\text{CH}_3\text{OCOCN}_2\text{H}$	photolysis	gas ~5 torr	$\lambda > 2200\text{\AA}$	>28

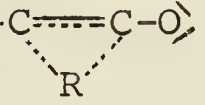
yields are decreased, particularly in a polar solvent;

- 3) in non-polar solvents, the oxirene yields increase with increasing wavelength whereas in polar solvent the reverse trend obtains;
- 4) no scrambling was observed upon using Michler's ketone as a triplet sensitizer or in thermolysis experiments;
- 5) auxiliary studies on the photolysis of dimethyl- and diphenyl-ketene-¹³C¹⁸O showed that the degree of oxirene participation is markedly lower than that from the corresponding diazoketones.

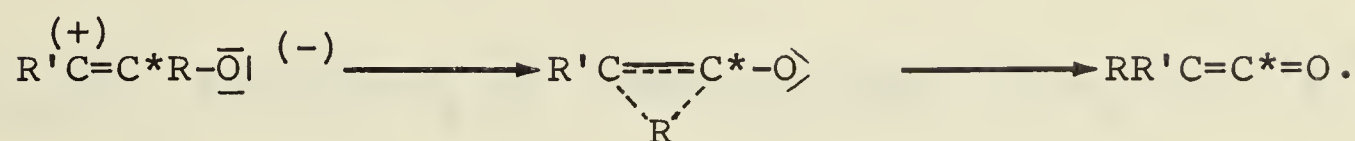
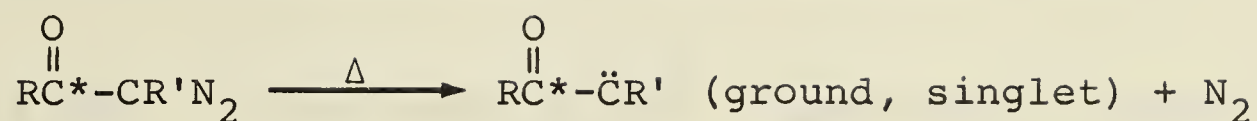
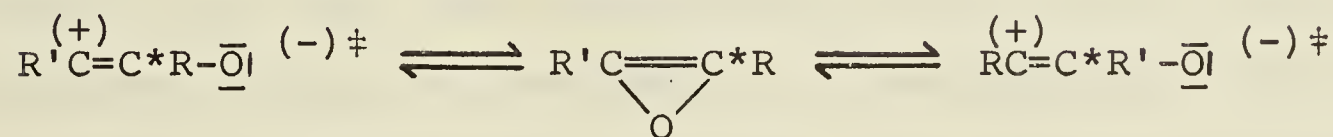
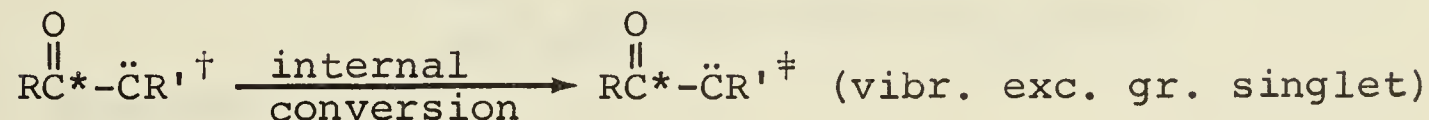
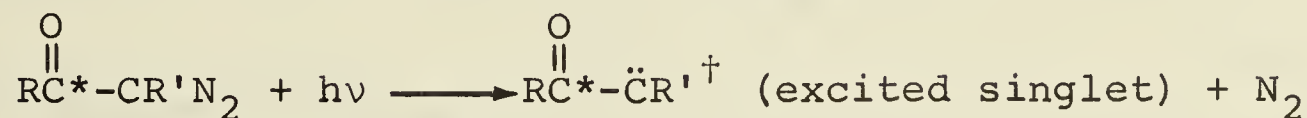
In the light of these results, it can be concluded that oxirene is indeed an important intermediate in the photochemical WR of simple α -diazoketones and in the photodecomposition of ketenes. It appears to be a characteristic photoproduct; oxirene formation occurs via a singlet reaction surface, and the carbene precursor must be in an energetic singlet state since the ground state carbene formed in thermolysis does not form oxirene.

The reaction surfaces involved in these rearrangements were elucidated by an Extended Hückel Molecular Orbital (EHMO) study²² on diazoethanone, 3-diazo-2-propanone, 2-diazo-3-propanone, 3-diazo-2-butanone, their decomposition products, the oxirenes, ketenes, and related

intermediates. The salient features are:

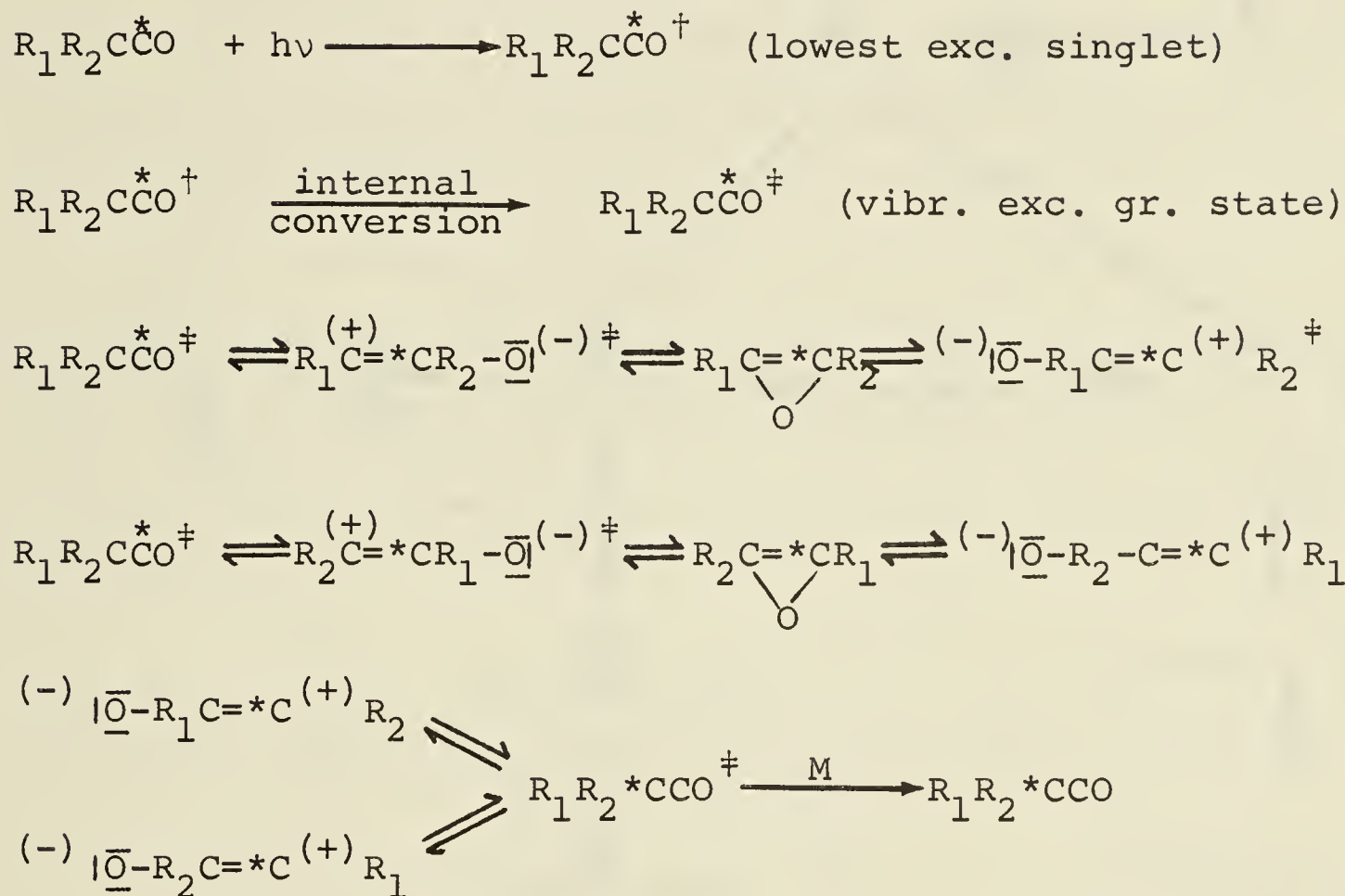
- 1) the singlet excited ketocarbene formed in photolysis has sufficient energy to isomerize to oxirene but since this is a symmetry-forbidden process, it must undergo rapid internal conversion to a vibrationally excited ground state from which the transformation takes place;
- 2) the valence isomer of the carbene, the zwitter ion $RC^+=CR-\bar{O}|^-$, appears to be considerably more stable than the carbene although the actual magnitude may be overemphasized by the EHMO method;
- 3) the zwitter ion can transform smoothly in either of two directions in an orbital symmetry allowed process to oxirene or to ketene via a bridged intermediate, $R-C \cdots C-O$

- 4) the transition state for ketene formation lies only slightly below the energy of the carbene but more than 30 kcal/mole below the oxirene state. Therefore, only those carbenes formed by photochemical excitation have sufficient energy to isomerize to oxirene prior to ketene rearrangement.

These results can now be formulated into the following schemes:

ThermolysisPhotolysis

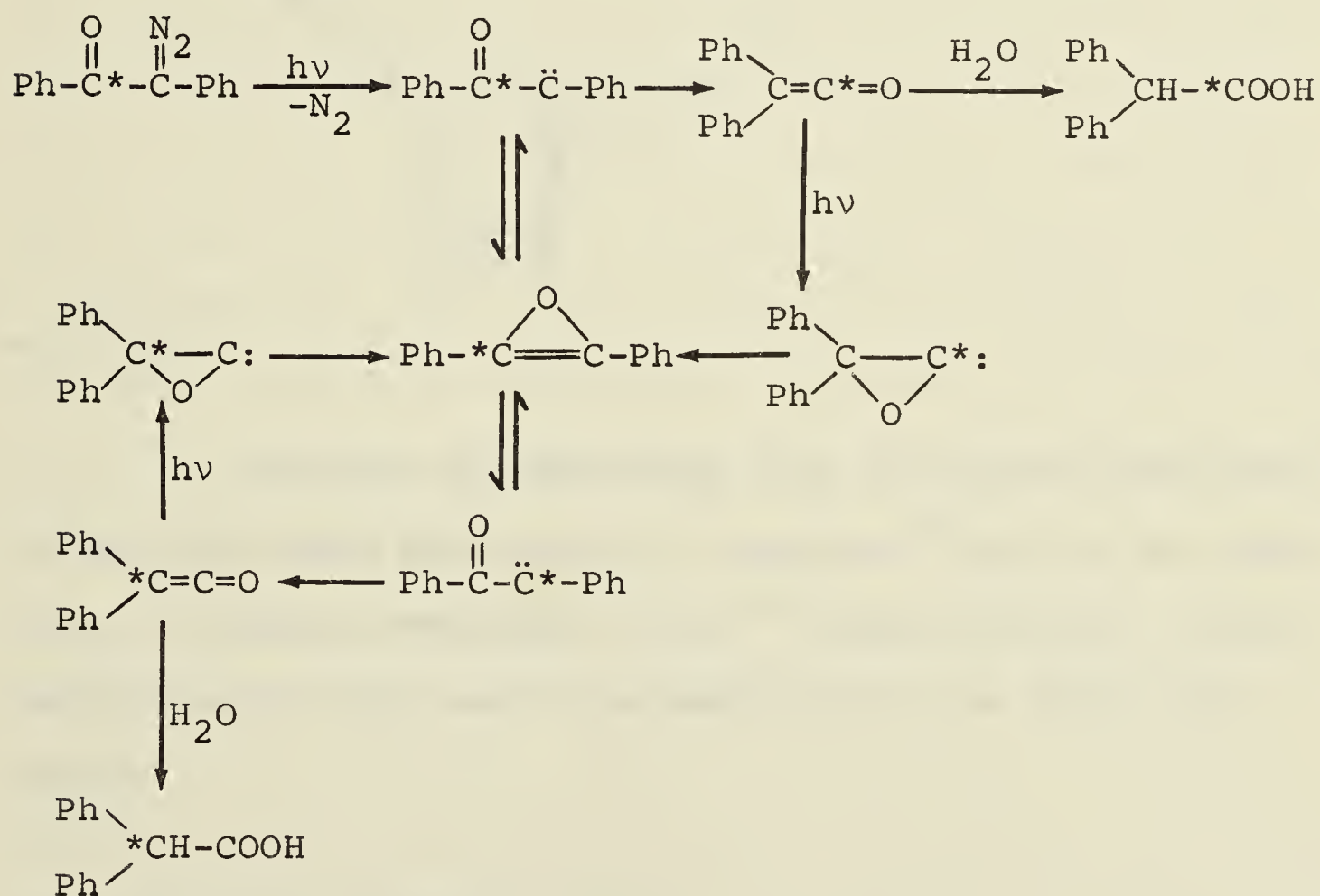
In the case of ketenes, where oxirene participation is small, deactivation and decomposition compete with rear-

rearrangement. The proposed reaction sequence is



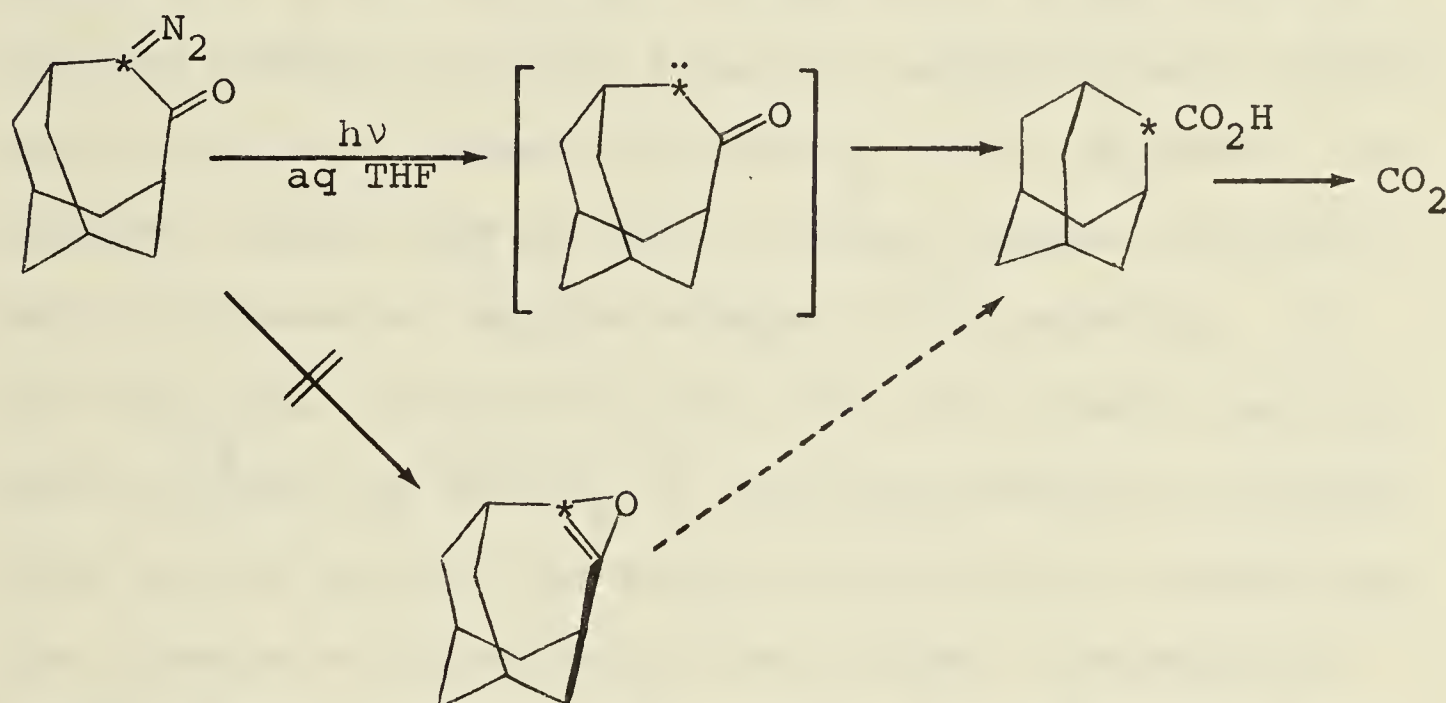
The existence of oxirenes as reactive transients in the WR of α -diazoketones has also been verified by other workers. Maltin and Sammes⁴¹ used a chemical method, based on the fact that ketocarbenes which contain adjacent methylene groups can rearrange to α,β -unsaturated ketones in addition to undergoing the WR. The degree of oxirene involvement in the rearrangement sequence of 3-diazo-4-heptanone was estimated to be 86%:

z11- ^{13}C O was decomposed thermally, photochemically and by electron impact and scrambling was only observed in photolysis. The effect of solvent polarity was investigated by changing the water-dioxane ratios and the degree of oxirene participation was also found to decrease with increasing solvent polarity. The authors proposed a tentative reaction scheme in which the varying degrees of scrambling observed presumably result from the competition between secondary oxirene formation in the ketene and the ketene-water reaction:



The intermediacy of oxirene in the photolytic WR of simple α -diazoketones has been proven conclusively.

Very little work has been done, however, on cyclic systems. Majerski⁴³ found only 0.9% scrambling in the photolysis of 5-diazo-[5-¹⁴C]-4-homoadamantone and concluded that the oxirene structure is not involved in the WR of strained, polycyclic systems:



* = ¹⁴C

Oxirene intermediates have also been postulated in the gas phase photolysis of ketenes,⁴⁴ and in the addition of singlet methylene to CO;⁴⁵ significantly, triplet methylene did not lead to scrambling in the final products.

1.2 Aim of the Present Work

Although the intervention of oxirenes as transient intermediates in the photochemical WR of α -diazoket-

ones has now been firmly established, there are several mechanistic and structural aspects of the reaction to be investigated.

It is seen from Table 1 that the highest yield of oxirene obtains from symmetrically substituted diazo compounds. It was therefore decided to examine the substituent effects by using a pair of asymmetrically substituted substrates, namely $\text{CH}_3^*\text{COCHN}_2$ and $\text{CH}_3\text{CN}_2^*\text{CHO}$. Substituent effects may be due to various causes, exerting their influence at various stages of the reaction. It was hoped that by starting with the two isomeric ketocarbenes $\text{CH}_3\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\ddot{\text{C}}\text{H}$ and $\text{HC}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\ddot{\text{C}}\text{H}_3$ it would be possible to decide which is the controlling step in the isotopic scrambling, ring closure or formation of the bridged intermediate. A complimentary study on the extent of scrambling in the gas phase photolysis of $\text{CH}_3\text{CH}=\text{C}=\text{O}$ was also performed. The influence of phase on the scrambling reaction in the diazo-ketones was examined.

Another problem with regard to the mechanistic details of oxirene formation is the role of singlet versus triplet state carbenes. With the exception of the photolysis of diazoacetophenone, kinetic mechanistic data on all reactions concordantly point to the presence of singlet state carbenes in the WR of diazoketones. In order to elucidate this question it was decided to reinvestigate the

photolysis and triplet sensitized photolysis of diazoacetophenone. Both polar and nonpolar solvents were used.

CHAPTER 2

EXPERIMENTAL

2.1 Apparatus and Instrumentation

Conventional apparatus and instruments were used throughout this work. A brief description of each and a general outline of some experimental techniques will be given.

A High Vacuum System was used for analysis of gaseous products, degassing samples and low temperature distillations. It was equipped with mechanical and mercury diffusion pumps, allowing pressures of the order of 10^{-6} torr. The analytical system consisted of a U-trap distillation train, a Toepler pump with a mercury float valve, McLeod and Pirani gauges, a gas burette and a gas chromatographic (g.c.) analysis system. The g.c. analysis system consisted of a Gow-Mac TR2B thermal conductivity detector, a Gow-Mac 9999-C power supply and a Sargent SR recorder. The g.c. detector outlet was connected with a vertical spiral trap train for collecting gaseous products as they were eluted from the g.c. column. Products were then collected in an evacuated break-seal valve for identification.

The Photolysis Lamp Assembly consisted of a

Hanovia 450 W medium pressure mercury lamp (No 679 A36) connected to a voltage transformer and a cylindrical cut-off filter sleeve surrounded by an immersion well built of quartz with a cooling jacket connected to a cold water line⁴⁶ (Fig. 1a). The photolysis reaction vessel (Fig. 1b) consisted of a quartz tube with a standard 12/30 joint to permit attachment to a vacuum type stopcock. The reaction vessel containing the sample was attached next to the immersion well and the entire assembly was placed in the water bath connected to an Ultra-thermostat, or to a cold water line (Fig. 1c), as desired.

Several different cylindrical filter sleeves were used, having the following transmissions:

Vycor 7910 (Hanovia No 512-27-114) $\lambda > 2200 \text{ \AA}$

Pyrex 7740 (Hanovia No 516-27-116) $\lambda > 2700 \text{ \AA}$

Uranium glass $\lambda > 3600 \text{ \AA}$

The high vacuum system was also used to degas samples.

In general, samples to be photolyzed in either the gas or liquid phase were thoroughly degassed by repeated thawing and condensation.

The Thermolysis Assembly used for thermal decomposition of substrates consisted of a quartz photolysis cell, 5 x 10 cm., fitted in an aluminium block furnace. The furnace was heated with pencil heaters and the temperature regulated with a Variac powerstat (Type 3PN116).

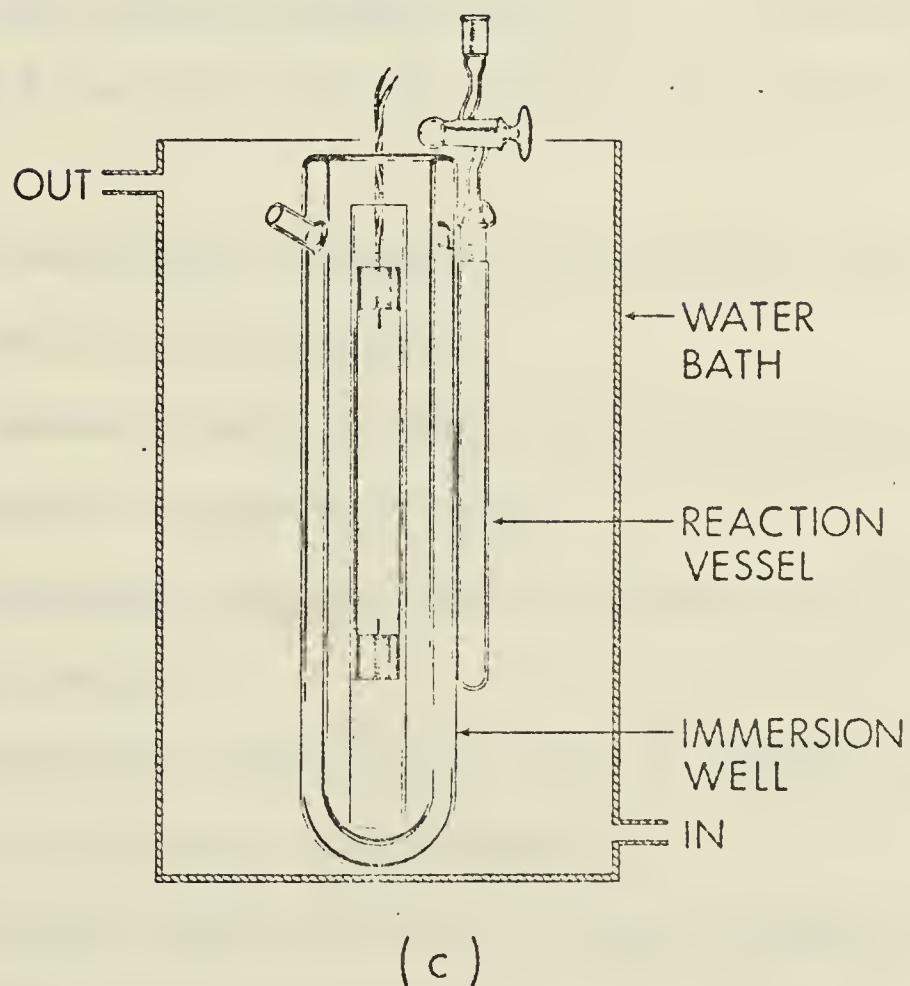
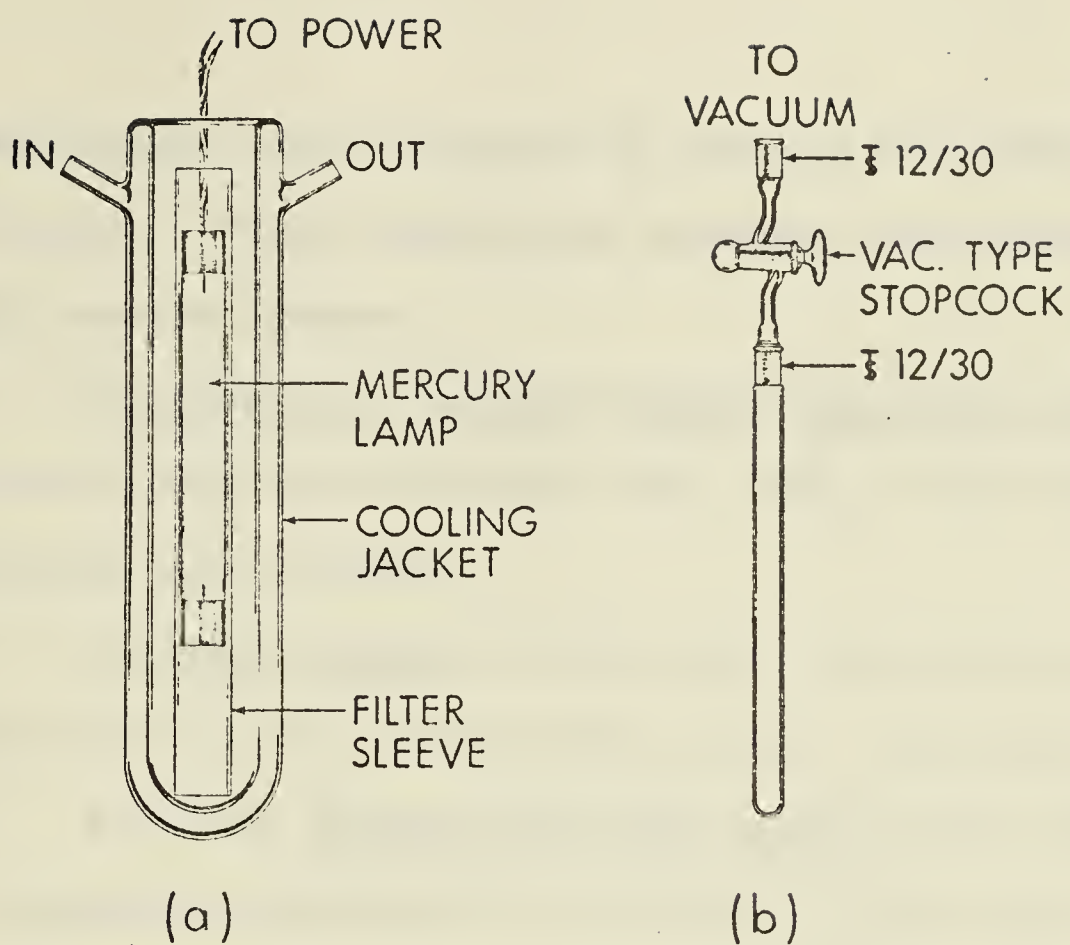


Figure 1. (a) Immersion well
(b) Reaction vessel
(c) Photolysis assembly

The temperature was monitored by the use of iron-constantan thermocouples. The thermolysis assembly was connected to the high vacuum system.

An Adiabatic annular teflon spinning band distillation column (Nester-Faust Mfg. Corp.) was used for purification of solvents.

A Fisher-Johns melting point apparatus was used for the determination of melting points (uncorrected).

Standard glass break-seal valves were used to collect gaseous products for analysis by mass spectrometry.

Gas Chromatography (g.c.). In addition to the g.c. unit of the high vacuum system, two more instruments were used:

a) an Aerograph Autoprep Model A-700, for purification of materials and products;

b) a Hewlett-Packard Model 5750 B, for qualitative and quantitative analytical work.

Spectral analyses were carried out on the following instruments:

a) ultraviolet absorption (u.v.) spectra were measured on a Cary 15 recording spectrometer;

b) infrared spectra (i.r.), were recorded on a Perkin-Elmer PE-700 spectrophotometer;

c) nuclear magnetic resonance (n.m.r.) spectra were recorded on Varian A 60 and Varian A 100 spectrometers.

The Varian A 100 instrument was used for the identification of products isolated in trace quantities as well as for qualitative and quantitative work with labelled ^{13}C compounds. The n.m.r. data complemented mass spectral analyses in the localization of the ^{13}C carbon isotope in the compound and the calculation of isotope enrichment.

d) Mass spectra (m.s.) were recorded on three different spectrometers:

i) an A.E.I. MS 9 high resolution mass spectrometer was used for accurate mass measurements;

ii) an A.E.I. MS 12 coupled with g.c. was used for analysis of liquid reaction mixtures, and

iii) an A.E.I. MS 2 was used for analysis of gaseous products collected in break-seals from the high vacuum system g.c. separations.

In this work the extent of isotopic scrambling was determined for gas and liquid phase photolyses, as well as in thermolyses of diazocompounds and methylketene. Two different techniques were employed, depending on whether the experiments were conducted in the gas or liquid phase.

In the case of the gas phase photolyses of diazo compounds and methylketene, the noncondensable gases were collected in an evacuated tube, and analyzed on the high resolution mass spectrometer (MS 9). After subtracting

the background, the content of ^{13}C in the $^{12}\text{CO}/^{13}\text{CO}$ mixture was determined and the scrambling was calculated by comparing this number with the total ^{13}C content of the starting material. In the case of methylketene, which was partially scrambled during the pyrolysis of parent diazopropanone, the calculations were more complex, and participation from ^{13}C on both C-1 and C-2 had to be included.

Liquid phase photolyses of 2-diazopropionaldehyde- ^{13}C O and α -diazoacetone- ^{13}C O were performed in methanol and the major product was methyl propionate. The ester was analyzed by n.m.r. spectroscopy (Varian A 100) and where scrambling occurred, a $J_{\text{C}^{13}\text{-H}} = 120$ cps in the $-\text{*CH}_2$ coupling was observed in addition to the coupling $J_{\text{C}^{13}\text{-OCH}_3} = 4$ cps. The scrambling was calculated by comparing the amount of ^{13}C in the *C=O group before and after photolysis or thermolysis.

Quantitative analyses of gaseous and liquid products were carried out using g.c. The gaseous products were analysed by the g.c. unit coupled with the high vacuum system; the detector response was calibrated with authentic samples. The liquid products were analyzed by g.c. using an injection technique and the Hewlett-Packard research gas chromatograph. Injections were made with a Beckman 75100 Micro Liquid Sampler having a reproducibility of 0.1 to 0.5%. Absolute yields were determined from calibration curves using standard solutions.

2.2 Materials

2.2.1 Preparation of 1,1-Diethoxypropane-1-¹³C, II

II was prepared from propionaldehyde-1-¹³C, 90% ¹³C, (Merck, Sharp and Dohme) and ethanol by the general procedure of A. I. Vogel.⁴⁷ To a cooled mixture of ethanol 4.3 g (0.093 moles) and dry CaCl₂ 0.9 g (0.0081 moles), 2.7 g (0.0458 moles) of propionaldehyde-1-¹³C was added. The mixture was shaken 0.5 hr and kept at room temperature for 24 hr. The top layer was separated, washed with water, dried and distilled. The yield was 2.95 g (0.022 moles) or 48% based on the starting material. The product was identified by comparing the i.r. spectrum with that of an authentic sample. II was then used as a starting material for the preparation of 2-methyl-3-dimethylaminoacrolein-¹³CO.

2.2.2 Preparation of 2-methyl-3-dimethylaminoacrolein-¹³CO, III

III was prepared as described by Z. Arnold⁴⁸ with slight changes in the procedure.

Phosgene gas was bubbled through a cool solution of 4.1 g (0.056 moles) dimethylformamide in 9 ml of ethylenedichloride until the weight of the reaction mixture had increased by ~2.5 g. The almost solidified adduct was

diluted with 4.5 ml ethylene dichloride then 2.95 g (0.022 moles) of II was added, with cooling and mixing. When the reaction was completed, the mixture was heated for 15 min at 70° and then 9 g of ice were added. After that, 18 ml of saturated potassium carbonate solution was added with continuous mixing. Ethylene dichloride was removed in a Rotavapour Büchi apparatus and the product extracted with a 3 x 5 ml benzene:ethanol (2:1) solution. The extracts were combined and dried with anhydrous sodium carbonate. The solvent was removed in the Rotavapour Büchi apparatus and the product collected by vacuum distillation ($\sim 90^\circ/0.1$ mm). The yield was 1.5 g (0.0132 moles) or 60% based on II, or 29%, based on the starting material, propionaldehyde.

Analytical data:

b.p. 90-100°/0.2 mm.

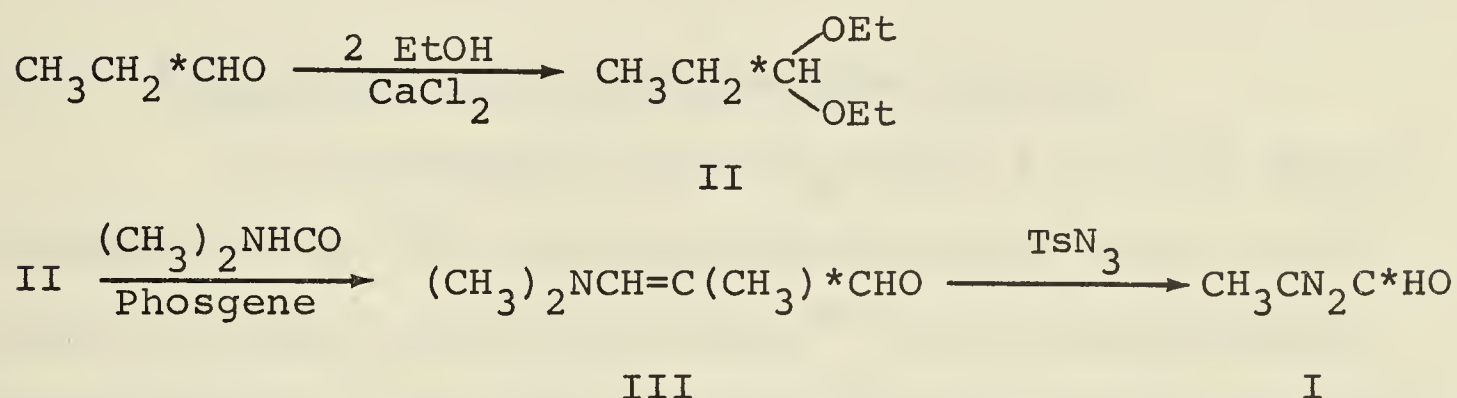
n.m.r. (CDCl_3), unlabelled: δ 8.90, s, 1H, CH=O
6.60, s, 1H, CH=C
3.17, s, 6H, $(\text{CH}_3)_2\text{N}$
1.93, s, 3H, $\text{CH}_3\text{-C=}$

i.r. (CCl_4): 1605 cm^{-1} (C=O), 1650 cm^{-1} (C=C), 2740 and 2840 cm^{-1} (CO-H).

Labelled III was identified by comparison of the i.r. spectrum with that of the authentic unlabelled compound.

2.2.3 Preparation of 2-diazopropionaldehyde-¹³CO, I

I was prepared by the procedure of J. Kucera,⁴⁹ according to the following scheme:



To an excess of p-toluenesulphonyl azide (TsN₃)⁵⁰ 6.0 ml, 1.5 g (0.0132 moles) of III was added at 0° with continuous stirring. The reaction mixture was then left to stand for 2 hr at room temperature. The product was distilled at ~0.1 mm and trapped at -64°C (chloroform slush). The crude product was purified on the Autoprep A-700 g.c. using a 5', 1/4", 20% SE-30 column at 45° and He flow of 60 cc/min. The yield was 0.24 g (0.0028 moles) or 21.3% based on III, or 12.7% based on propionaldehyde.

Analytical data:

u.v. (cyclopentane): λ_{max} 248 m; (ϵ = 9.48)

λ_{max} 285 m; (ϵ = 6.92)

i.r. (neat): 2125 cm⁻¹ and 2250 cm⁻¹ (C=N₂)

n.m.r. (CCl₄): δ 1.87, s, 3H

9.55, t, 1H

m.s: $\underline{m/e}$ 28 (base peak); 84 (parent); 56 (P-N₂)

The % ¹³C in the carbonyl group was found to be 30.2% by n.m.r. spectroscopy.

2.2.4 Preparation of α -diazooacetone-¹³CO, IV

IV was prepared from CH₃*COONa 5 g (0.06 moles) (Prochem, 91.2% ¹³C) which was treated with 3 ml (0.033 moles) of POCl₃ to give CH₃*COCl,⁴⁷ 1.4 g (0.018 moles). Acetyl chloride was then treated with five-fold excess of diazomethane⁵¹ in diethyl ether solution. After the reaction was completed, the solvent was removed in the Büchi apparatus and crude IV subjected to low temperature distillation in vacuo. The product was a yellow liquid, yield 1.0 g or 19.6% based on starting material.

Analytical data:

i.r. (neat): 1600 cm⁻¹ (C=O); 2125 cm⁻¹ and 2250 cm⁻¹ (CN₂)

n.m.r. (CCl₄): δ 2.04, t, 3H, -CH₃-*CO
5.18, d, 1H, -CHN₂

m.s: $\underline{m/e}$ 27 (base peak); 85 (parent); 57 (P-N₂);
44 (P-CHN₂); 15 (P-*COCHN₂)

The n.m.r. and mass spectra indicated 86.2% ¹³C on the carbonyl group.

2.2.5 Preparation of methylketene- ^{13}C O, V

Although many synthetic methods are known for the preparation of ketenes,⁵²⁻⁵⁴ the most convenient route for the preparation of labelled methylketene is the pyrolysis of IV at 180° in a high vacuum flow system.

Pyrolysis was carried out in the thermolysis assembly as described in the preceding section 2.1. The noncondensable gases were pumped out continuously during decomposition of IV. Methylketene- ^{13}C O was collected at -196° and non-decomposed IV and other heavy products were separated at -100° (methanol slush). Methylketene- ^{13}C O was identified by m.s. and by n.m.r. spectroscopy after quenching with methanol in the dark and at room temperature.

Analytical data:

b.p. -46°/760 mm⁵³

m.s. (unlabelled): $\underline{m/e}$ 56 (base peak); 56 (parent);
28 (P-CO); 27 (P-HCO); 26 (P-H₂CO)

n.m.r. (CCl₄) of methyl propionate:

δ 7.20, t, 3H, $^{14}\text{CO-OCH}_3$, J=4 cps

4.50, m, 2H, -CH₂

4.50, m, J₁₃C-H (-*CH₂) =120 cps

2.20, m, 3H, -CH₃, J₁₃C-CH₃ =5 cps

crude product was purified by g.c. (Autoprep A-700) on a 20% SE-30 column.

Analytical data:

n.m.r. (CCl_4): δ 7.40-7.90, m, 5H, Ph-CO

2.43, m, 1H, -CH

1.35-1.85, m, 10H, $-\text{C}_6\text{H}_{10}$

m.s.: $\underline{m/e}$ 105 (base peak); 200 (parent); 157 (P-43);
77 (P-123).

2.2.8 Preparation of bicyclohexenyl, VIII

VIII was prepared by the method of Berlande⁵⁶ from 3-chlorocyclohexene and ethyl bromide in the presence of magnesium. The product was purified by distillation at reduced pressure.

Analytical data:

i.r. (neat): 3030 cm^{-1} (=CH); 1450 cm^{-1} (C=C)

m.s.: $\underline{m/e}$ 81 (base peak); 162 (parent); 80 (B-H);
161 (P-H)

VIII was also used as a reference compound in the identification of products from the photolysis of diazoacetophenone in cyclohexene.

2.3 Methods

2.3.1 Photolyses

The photolyses of 2-diazo-1-propionaldehyde- ^{13}CO , I, and α -diazoacetone- ^{13}CO , IV, were studied in the gas phase and in methanol solution; the photolysis of methylketene- ^{13}CO , V was examined in the gas phase only.

The gas phase photolyses of I and IV were performed employing a Vycor 7910 cut-off filter sleeve. The bottom of the reaction vessel (Fig. 1b) was wrapped with aluminium foil to ensure that photodecomposition took place in the gas phase only. The samples were degassed prior to each photolysis and the lamp prewarmed for 30 min. The irradiation time does not represent the time necessary to photolyze the diazocompound completely, therefore the yields of products are based on the amount photolyzed, i.e. on the nitrogen yields. The products were analyzed by the Gow-Mac g.c. unit. Noncondensable gases were analyzed using a 7' Molecular Sieve (5A) column at 80° and He flow of 60 cc/min. The second fraction of volatile products collected at -130° (n-pentane slush) was analyzed on 6' Silica Gel high activity column at room temperature and He flow of 60 cc/min. The remaining third fraction was collected by room temperature distillation and analyzed on a 6' Tricresyl Phosphate (TCP) column at 60°

and He flow of 60 cc/min. For m.s. analysis the products were trapped after separation on the g.c. column. The total amounts of products in each fraction were measured in a gas burette. For the measurement of the extent of isotopic scrambling, the noncondensable gases were collected in an evacuated tube and analyzed by high resolution mass spectrometry (A.E.I. MS 9).

Methylketene- ^{13}C O was photolyzed in the gas phase at 20°, using a Vycor 7910 cut-off filter sleeve. Noncondensable gases were analyzed by g.c. using a Molecular Sieve (5A) column, and the amount of scrambling determined by high resolution mass spectrometry. The remaining fraction was analyzed by g.c. using a high activity silica gel column under the same conditions as described in section 2.3.1.

Diazo compounds I and IV were also photolyzed in methanol solution. Weighed amounts of substrate and solvent were degassed then photolyzed at 40°, using a Vycor 7910 filter sleeve for 30 min. The reaction vessel above the liquid surface was wrapped with aluminium foil. The irradiation time was carefully chosen by a number of trials in order to avoid secondary photolysis of the reaction products and at the same time to ensure complete photodecomposition of I and IV. The volatile products were collected in two fractions on the high vacuum system. The

first fraction of noncondensable gases was analyzed by g.c. using a 7' Molecular Sieve (5A) column at 80° and He flow of 60 cc/min. The second fraction was collected at -130° and analyzed by g.c. using a high activity silica gel column at room temperature and He flow of 60 cc/min. The total volume of each fraction was measured in the gas burette prior to g.c. analysis. The remaining liquid mixture was analyzed by g.c. (Hewlett-Packard 5750 B) using a 4' 1/8" Poropak Q column at 190° and He flow of 60 cc/min. Since the yield of carbon monoxide from the liquid phase photolysis was very low, the extent of isotopic scrambling was determined from methyl propionate, the major product of the reaction. Methyl propionate was separated from the excess solvent by the Gow-Mac g.c. unit and analyzed by n.m.r. (Varian A-100).

2.3.2 Thermolyses

The thermal decompositions of I and IV in the vapour phase were examined briefly, in part to generate labelled methylketene. The diazocompounds were decomposed in a flow system in vacuo. The compound was placed in a cold finger of the quartz cell, and the cell inserted into the aluminium block heater. The temperature was then set at ~180° and the liquid nitrogen trap removed. As the vapours decomposed in the furnace they were pumped into the

high vacuum system. Unreacted substrate was collected at -100° , volatile products at -196° , and noncondensable gases were pumped out. The fraction condensable at -196° was quenched with methanol in the dark and the resulting ester, methyl propionate, analyzed by n.m.r. after g.c. separation from the solvent.

2.3.3 The direct and sensitized photolysis of α -Diazoacetophenone, VI

VI was photolysed in the liquid phase only, using methanol, i-propanol and cyclohexene as solvents.

a) Direct photolysis

The direct photolyses were carried out in the same photolysis assembly as described in preceding section. Methanol and i-propanol were freshly distilled on a spinning band column. Cyclohexene was purified on an Alumina column, dried over potassium hydroxide pellets and distilled on a spinning band. The distillate was tested for the presence of peroxides with an aqueous solution of ferrous ammonium sulphate. A weighed amount of VI was placed into the photolysis vessel (Fig. 1b) together with required amount of solvent. Then the tube was degassed, and irradiation performed at 20° . When methanol and i-propanol were used as solvents two different filter sleeves were

employed, which also required different times of irradiation in order to ensure complete photodecomposition, yet avoid secondary photolysis. The irradiation with Vycor 7910 required 1 hr, whereas with Pyrex 7740, 1.5 hr. The irradiations in cyclohexene were carried out with a Pyrex 7740 filter sleeve, and the required time was 1 hr. Non-condensable gases were analyzed by g.c. using a 7' Molecular Sieve (5A) column at 80° and He flow of 60 cc/min. The total volume was measured in the gas burette. The methanol solution was analyzed by g.c. using a 15' 1/8" 15% SE-30 column (Hewlett-Packard 5750 B) at 150° and He flow of 60 cc/min. The i-propanol solution was analyzed on the same column but at 200°. The cyclohexene solution was analyzed by g.c. using a 5' 1/8" 10% DEGS (Diethyl glycol succinate) column with temperature programming in the range 70-150°; He flow was 60 cc/min.

A solid product was separated from the solvent by evaporation followed by partial dissolution in diethyl ether; the remaining insoluble crystals were then analyzed by standard techniques.

b) Sensitized photolysis

The photolysis of α -diazoacetophenone was also examined in methanol, i-propanol and cyclohexene solutions in the presence of a triplet sensitizer. Michler's Ketone

(MK) which has a large extinction coefficient at $\lambda_{\text{max}} = 366 \text{ m}\mu$, $\epsilon = 33600$, was used as a triplet photosensitizer. In the case of methanol and i-propanol, saturated solutions of MK were used; in the case of cyclohexene an excess of solid MK was added to the solution. The irradiations were performed at 20° with a Uranium glass filter sleeve. It was observed that, in contrast to direct photolysis, the time required for complete photodecomposition was very long. Therefore smaller amounts of VI were used. Product analyses were carried out in the same way as in direct photolysis with one exception. Recovery of the solid from cyclohexene solutions was not attempted since the concentrations were too low and solid MK was present.

CHAPTER 3

RESULTS

3.1 2-Diazopropionaldehyde-¹³CO

3.1.1 Photolysis in the gas phase

Samples of 100-200 μ moles of I were degassed and allowed to equilibrate to 40°. The liquid portion of the tube was wrapped with aluminium foil and the vapour was irradiated with Vycor filtered light. Noncondensable gases were analysed by g.c. and high resolution mass spectrometry and shown to consist of N₂, CO and small amounts of H₂ and CH₄. The condensable products which consisted of C₂H₄ and smaller amounts of acrolein, C₂H₂, C₃H₈, C₂H₆ and C₃H₆ were separated into two fractions by distillation at -130°. The average yields of four experiments are summarized in Table 2.

The degree of scrambling was calculated as follows. The ratio ¹²CO/¹³CO in the high resolution background (Figure 2b) was subtracted from the ¹²CO/¹³CO ratio of the sample, Figure 2a, and the % ¹³CO in the sample was calculated. Since the enrichment in the starting material was 30.2%, then

$$\% \text{ scrambling} = [(30.2 - \%^{13}\text{CO})/30.2] \times 100$$

Table 2

Product Yields from the Gas Phase Photolysis of I^a

Product	% Yield ^{b,c}
carbon monoxide	18
hydrogen	1
methane	traces
ethylene	11
ethane	0.2
propane	1
acetylene	1
propylene	traces
acrolein	2
polymer	

a) Average of four experiments.

b) $\lambda > 2200 \text{ \AA}$

c) Calculated in terms of nitrogen produced.

The average $^{12}\text{CO}/^{13}\text{CO}$ ratio measured from the above experiments was 3.10. Thus, the ^{13}CO content was 24.4% and the degree of scrambling, 19.2%. Since the ^{13}C enrichment in the starting material was only moderate, it is estimated that the errors associated with these measurements are ca. 10% and possibly higher.

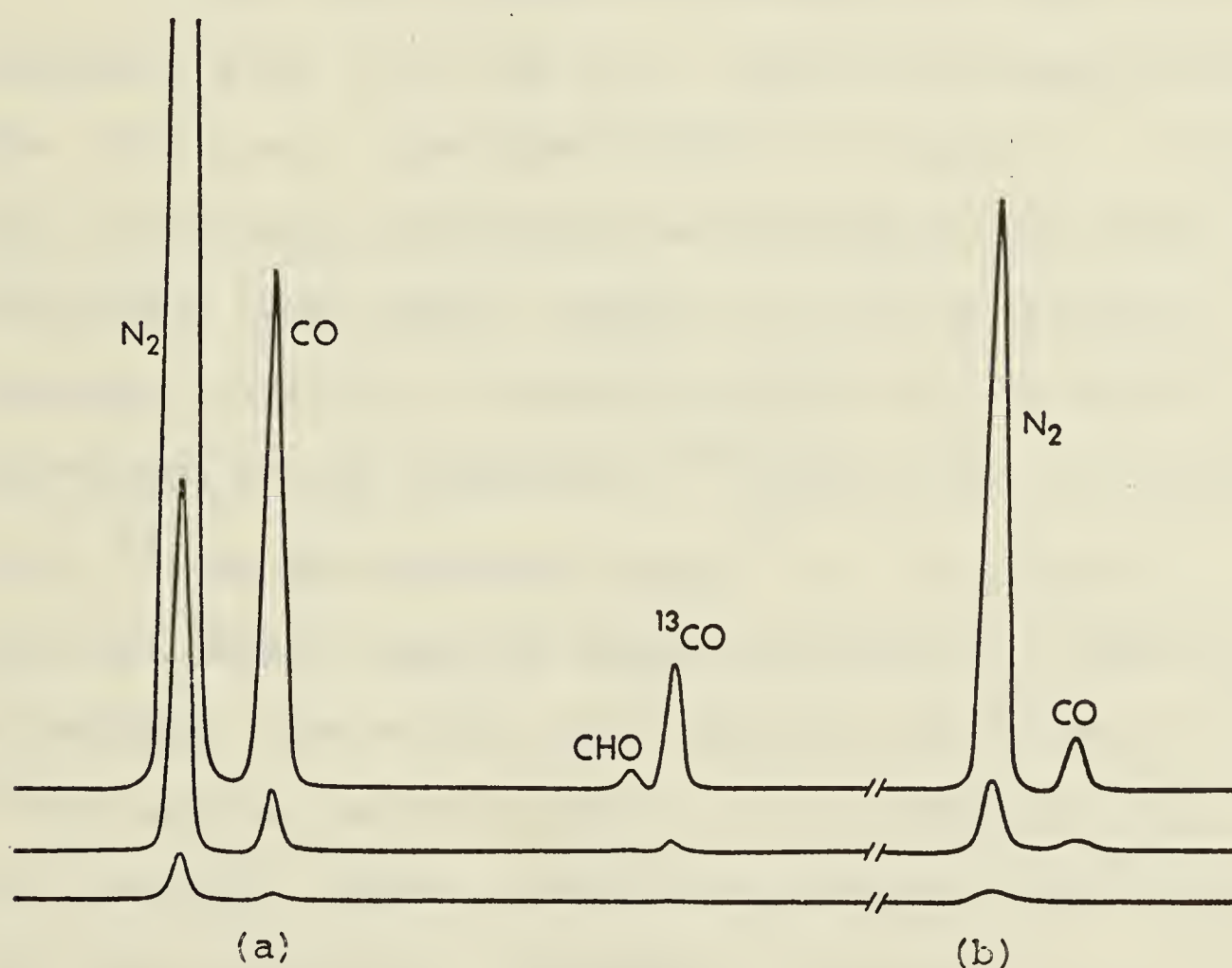


Figure 2

(a) High resolution mass spectrum of the noncondensable fraction from the photolysis of 2-diazopropionaldehyde- ^{13}CO .

(b) High resolution background.

3.1.2 Photolysis in methanol solution

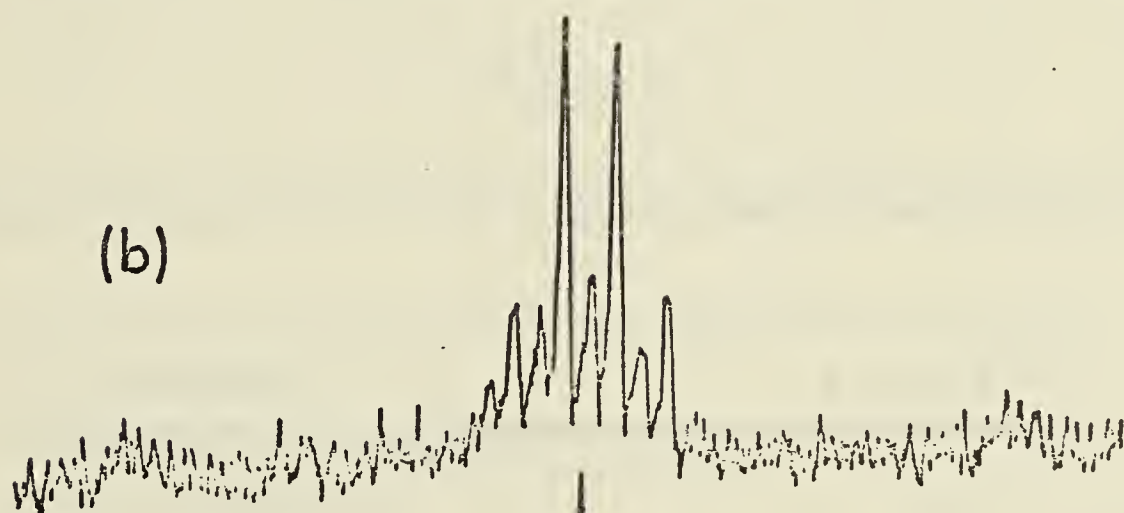
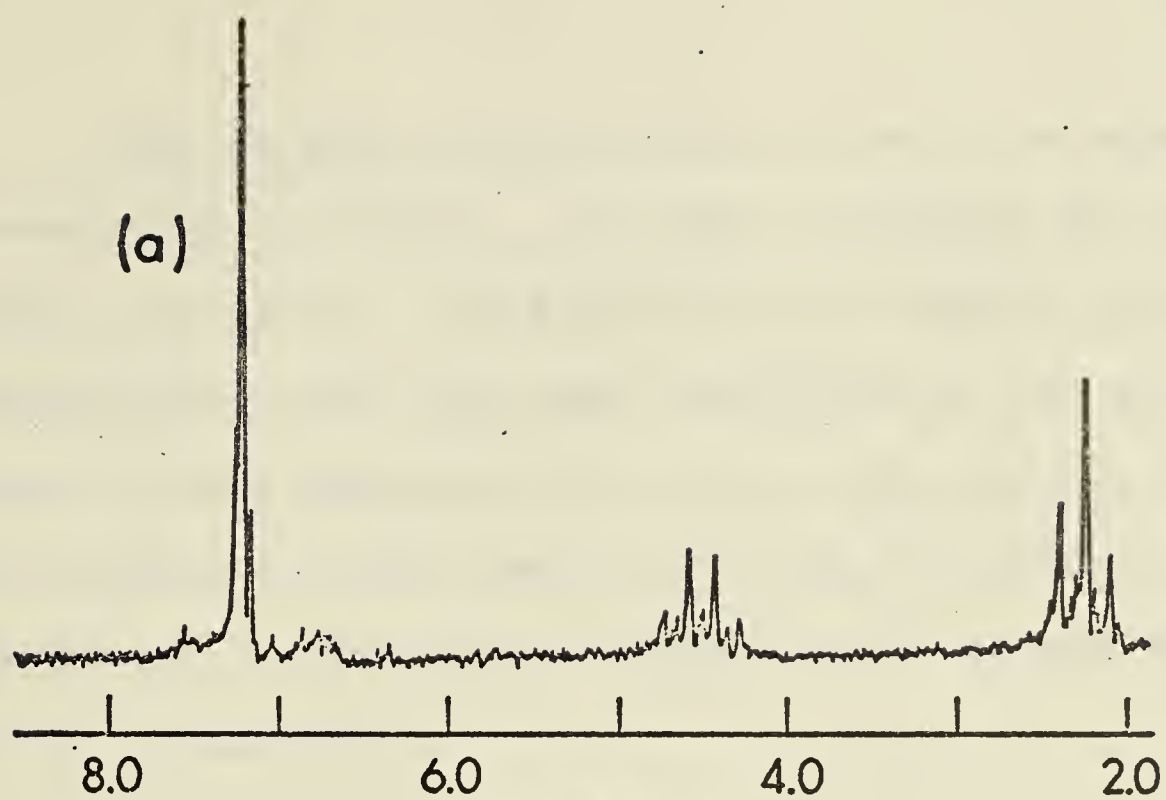
Degassed 1 cc samples of ~ 0.1 M methanol solutions of I were irradiated at 40° with Vycor filtered light. The noncondensable gases consisting of N_2 and small amounts of CO were separated and analysed by g.c. A small amount of ethylene was separated by low temperature distillation at -130° .

The major product was identified from the g.c. retention time, m.s. and n.m.r. spectra as methyl propionate. The n.m.r. spectrum is shown in Figure 3a. The extent of isotopic scrambling was determined from the high resolution $-OCH_3$ peaks, Figure 3c, and the extended $-CH_2-$ pattern, Figure 3b. The peaks heights and integrals corresponding to the coupling in $^{13}C-OCH_3$ (Fig. 3c) indicated 28.7% ^{13}C on the carbonyl group, i.e. a decrease of 1.5% from the parent compound which corresponds to about 5% scrambling. Due to the poor isotopic enrichment, the $^{13}C-H$ coupling on the carbon α to the carbonyl group was not observed; however, when the sensitivity was increased, some weak signals at a distance of 60 cps ($J_{^{13}C-H} = 120$ cps) from the $-CH_2-$ group were observed. These results indicate that a small amount of scrambling had taken place in the rearrangement but the results should not be viewed as quantitative since the errors associated with such small differences are large.

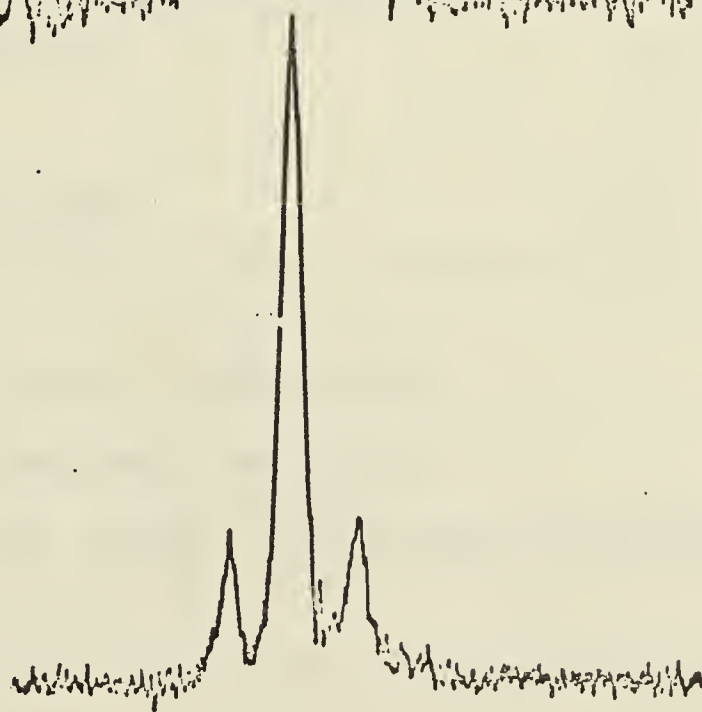


Figure 3

- (a) Nuclear magnetic resonance spectrum of labelled methyl propionate from the photolysis of 2-diazo-propionaldehyde- ^{13}C O in methanol.
- (b) Expanded n.m.r. spectrum of methylene portion of the methyl propionate.
- (c) Expanded n.m.r. spectrum of methoxy portion of the methyl propionate.



(c)



The average product yields from three experiments are summarized in Table 3. In order to assess the role of secondary reactions, ~0.2 M solutions of methyl propionate were photolyzed under the same conditions as the parent compound. Small amounts of CO, C₂H₄, C₂H₆ and CH₄ were formed, indicating that the CO and C₂H₄ detected in the photolysis of I arise from secondary photodecomposition of methyl propionate.

Table 3

Product Yields from the Liquid Phase Photolysis of I^a

Product	% Yield ^{b,c}
carbon monoxide	0.5
ethylene	0.5
methyl propionate	81

a) Average of three experiments.

b) $\lambda > 2200 \text{ Å}$; methanol solution.

c) Calculated in terms of nitrogen produced.

3.1.3 Thermolysis of I

The thermal decomposition of I was also investigated in the vacuum flow system at 180°. The product, methylketene, was quenched with methanol in the dark and the resulting methyl propionate was then subjected to n.m.r. analysis. The isotopic labelling of the carbonyl group was found to be 29%. Comparison of the ^{13}C content of the ketene with that of the corresponding I showed that a small degree of scrambling, ~5%, had occurred. But, as in the case of the liquid photolysis, the ^{13}C -H coupling on the carbon α to the carbonyl group was not observed.

3.2 α -Diazoacetone- ^{13}C O

3.2.1 Photolysis in the gas phase

Degassed samples of ~100 μmoles of IV were prepared as described in Section 3.1.1 and irradiated at 40° through a Vycor filter. The noncondensable gases were separated from the condensable products and analyzed by g.c. and high resolution mass spectrometry. A typical mass spectrum of the noncondensable fraction is shown in Figure 4, and the reproducibility of the measurements is indicated by the data in Table 4. The average degree of isotopic scrambling is $(20.5 \pm 3.8)\%$, well within the range of error of that from the gas phase photolysis of I.

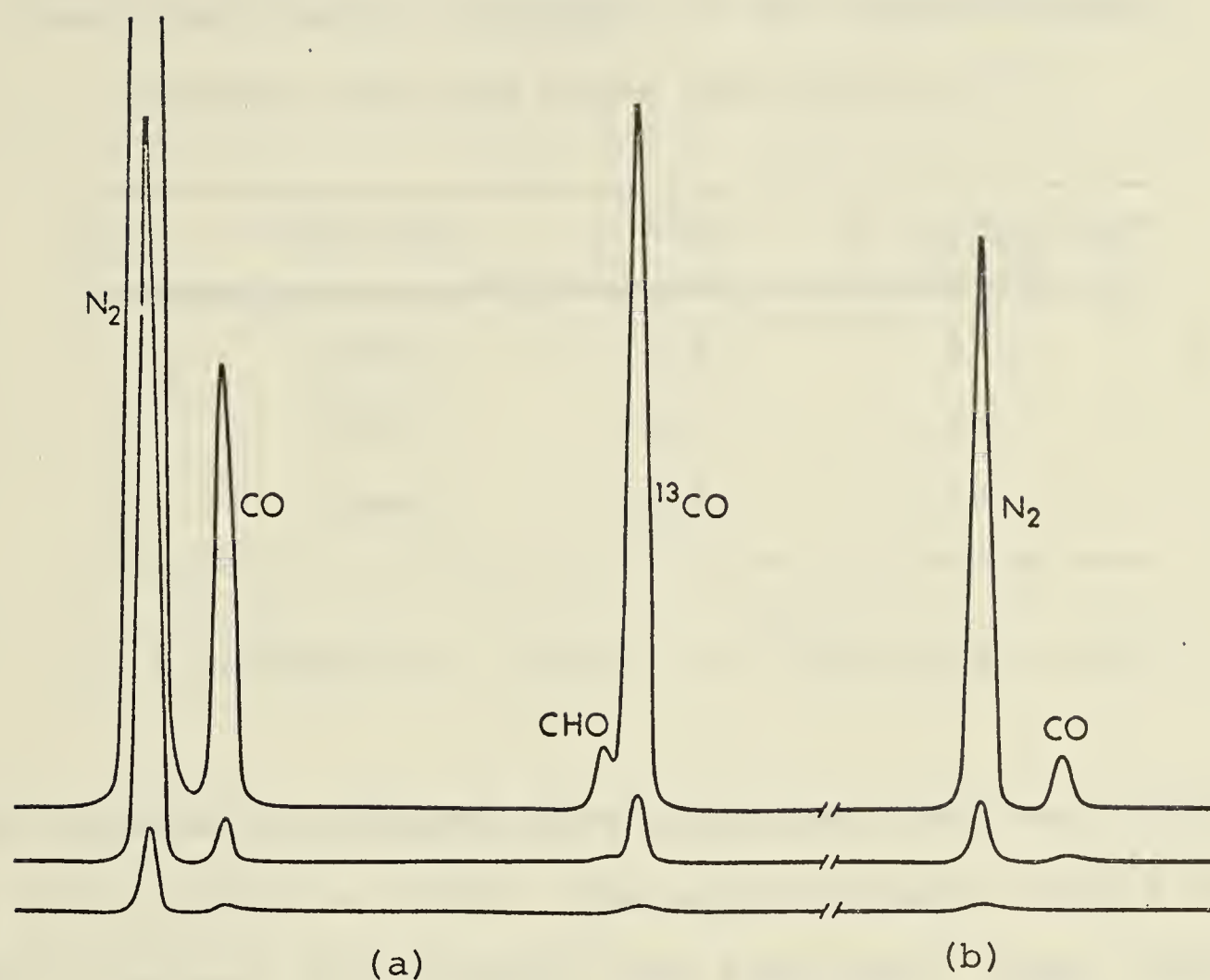


Figure 4

- (a) High resolution mass spectrum of the noncondensable fraction from the photolysis of α -diazooacetone- ^{13}CO .
- (b) High resolution background.

Table 4

Mass Spectrometric Analysis of the Noncondensable
Fraction from Gas Phase Photolysis of IV

Run	$^{12}\text{CO}/^{13}\text{CO}$	% ^{13}CO	% scrambling ^a
1	0.395	71.5	17
2	0.551	64.5	25
3	0.450	69.0	20

a) % scrambling = $[(86.2 - \% ^{13}\text{CO})/86.2] \times 100$.

The condensable products were separated into two fractions by distillation at -130° . The major products of the volatile fraction were ethylene and acetylene. Small amounts of ethane, propane and propylene were also detected as well as some acetone in the condensable fraction. A summary of these analyses is listed in Table 5.

3.2.2 Photolysis in methanol solution

Degassed 1 cc samples of ~ 0.1 M methanol solutions of IV were irradiated at 40° with a Vycor filter. The noncondensable gases consisted of nitrogen and small amounts of carbon monoxide. Small amounts of ethylene and ethane were detected by low temperature distillation at

Table 5

Product Yields from the Gas Phase Photolysis of IV^a

Product	% Yield ^{b,c}
carbon monoxide	14
hydrogen	1
methane	traces
ethylene	7
ethane	0.2
propane	0.7
acetylene	1
acetone	1
polymer	

a) Average of four experiments.

b) $\lambda > 2200 \text{ \AA}$.

c) Calculated in terms of nitrogen produced.

-130°, and are believed to originate from the secondary photolysis of methyl propionate (c.f. Section 3.1.2). The major component of the condensable fraction was methyl propionate, which was subjected to n.m.r. analysis for the determination of isotopic scrambling. A typical n.m.r. spectrum is shown in Figure 5. The ^{13}C -H coupling on the carbon α to the carbonyl group of the ester was clearly observed (Fig. 5b) and proves that scrambling had indeed occurred, but to a small extent. From the integrals of the ^{13}C -OCH₃ coupling signals, the ^{13}CO content was estimated to be 80.7%. Comparison of the ^{13}C content in the ester and the parent diazocompound IV showed that scrambling had occurred to an extent of 6.7%. A summary of analyses is listed in Table 6.

3.2.3 Thermolysis of IV

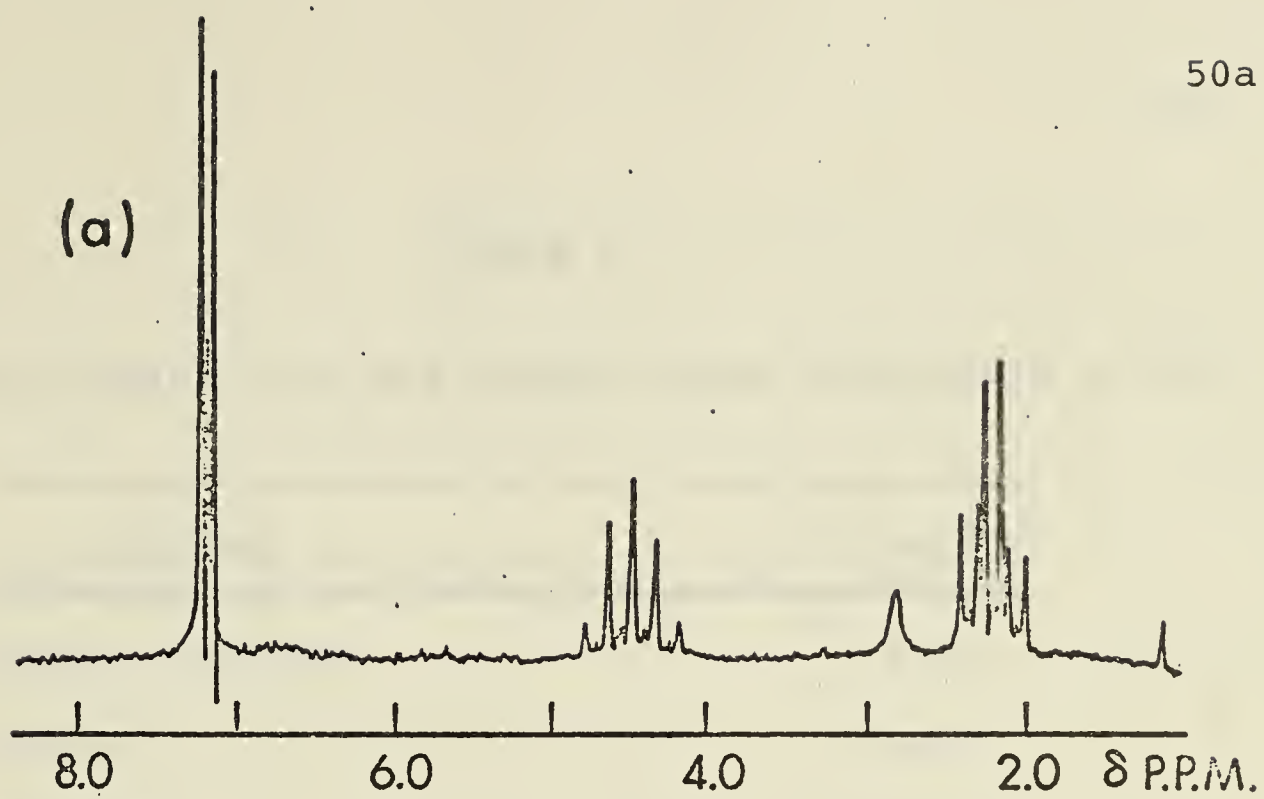
The thermolysis of IV was carried out at 180° in the vacuum flow system. The major product was methylketene, which was quenched with methanol in the dark at room temperature, and the resulting methyl propionate was analyzed by n.m.r. Similarly to the photolysis of IV in methanol, little scrambling had occurred, as was inferred from the intensity of the ^{13}C -H coupling on the carbon α to the carbonyl group of the ester. The ^{13}C content on



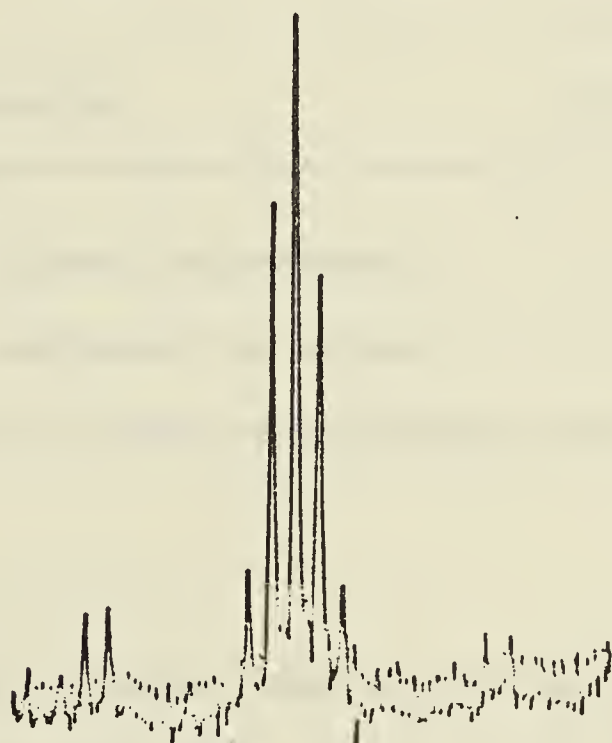
Figure 5

- (a) Nuclear magnetic resonance spectrum of labelled methyl propionate from the photolysis of α -diazoacetone- ^{13}C in methanol.
- (b) Expanded n.m.r. spectrum of methylene portion of the methyl propionate spectrum.
- (c) Expanded n.m.r. spectrum of methoxy portion of the methyl propionate spectrum.

50a.



(b)



(c)

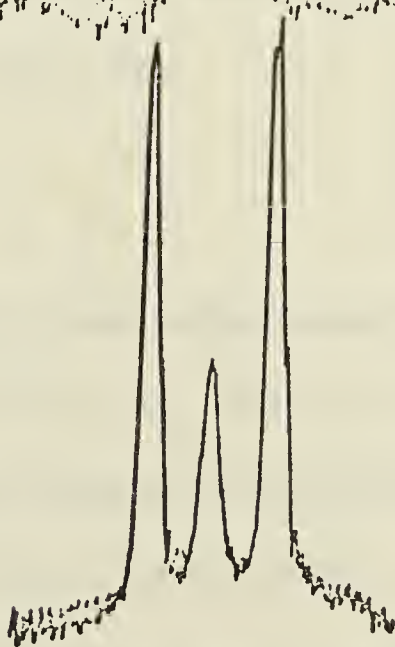


Table 6

Product Yields from the Liquid Phase Photolysis of IV^a

Product	% Yield ^{b,c}
carbon monoxide	0.2
ethane	traces
ethylene	~0.2
methyl propionate	94.0

a) Average of three experiments.

b) $\lambda > 2200 \text{ \AA}$; methanol solution.

c) Calculated in terms of nitrogen produced.

the carbonyl group of ester was 80.4%, which indicated an isotopic scrambling of 6.7%.

3.3 Methylketene

Methylketene was generated by the pyrolysis of neat α -diazoacetone-¹³C₂O, at 180° in a vacuum flow system. The degree of ¹³C enrichment was calculated from the n.m.r. analysis of methyl propionate (Section 3.2.3) and found to be 80.7% in the carbonyl position and 5.8% on the carbon atom α to the carbonyl group.

A degassed sample of V was photolyzed at 20° with Vycor filtered light for 6 hrs. The noncondensable gases were analyzed by g.c. and only carbon monoxide was detected. A portion of the CO was analyzed by high resolution mass spectrometry and found to consist of 68.8% ^{13}CO . The degree of scrambling, x, during the photolysis, was calculated from the following relation:

$$80.7 - 80.7x + 5.8x = 68.8$$

The average value of x was 16%.

The condensable fraction was analyzed by g.c. and found to consist of ethylene and acetylene. Table 7 shows the product yield averages of three experiments.

3.4 α -Diazoacetophenone

Preliminary experiments with unlabelled VI indicated that the acetophenone yields were much lower than those claimed by Padwa and coworkers⁹ or Hammond and coworkers.¹⁰ Since the yields of acetophenone were taken as a direct measure of the triplet state ketocarbene intervention in the reaction, it was decided to reinvestigate the photolysis and sensitized photolysis of VI in polar and non-polar solvents.

Table 7

Product Yields from the Gas Phase Photolysis of V^a

Product	% Yield ^{b,c}
hydrogen	~1
methane	traces
ethylene	48.0
ethane	4
propane	<0.1
acetylene	11
propylene	traces
polymer	

a) Average of three experiments.

b) $\lambda > 2200 \text{ Å}^\circ$.

c) Based on the amount of carbon monoxide produced.

3.4.1 Polar Solvents

The direct photolysis of VI was studied at 20° in methanol and i-propanol using Vycor and Pyrex filtered light. The triplet photosensitized decomposition was also studied using Michler's Ketone (MK). The results are summarized in Tables 8 and 9.

In the direct photolysis the yields of acetophen-

Table 8

Product Yields from the Direct Photolysis of VI in Polar Solvents^{a,b}

Product	<u>Vycor</u>				<u>Pyrex</u>			
	<u>MeOH</u>		<u>i-PrOH</u>		<u>MeOH</u>		<u>i-PrOH</u>	
	1	2	1	2	1	2	1	2 3 4
CO	1	1	0.7	0.8	0.2	0.3	0.3	0.3 -- --
PhCOCH ₃	traces	traces	2	2	--	traces	<0.5	<0.5 1 1
PhCH ₂ COO-R ^c	86	85	63	64	95	85	67	70 75 77
N ₂	99	99	96	97	99	98	96	98 97 98

a) Based on the amount of starting material used.

b) 10-15 mg/cc.

c) R=-CH₃ or -CH(CH₃)₂.

Table 9

Product Yields from the Sensitized Photolysis
of VI in Polar Solvents^{a,b}

Product	MeOH			i-PrOH	
	1	2	3	1	2
PhCOCH ₃	10	8	12	50	49
PhCH ₂ COO-R ^c	69	59	62	2	2
N ₂	98	97	96	98	98

a) Based on the amount of starting material used.

b) 4-8 mg/cc.

c) R=-CH₃ or -CH(CH₃)₂.

Table 10

Ester to Acetophenone Product Ratios

PhCH₂COO-R/PhCOCH₃^a

Direct				Photosensitized		
Vycor		Pyrex		Uranium Glass		Ref.
MeOH	i-PrOH	MeOH	i-PrOH	MeOH	i-PrOH	
170	32	170	95	7.2	0.044	this work
-	-	>300	2.5	7.3	<0.003	9

a) R=-CH₃ or -CH(CH₃)₂.

one are small suggesting that triplet state ketocarbene is not an important intermediate in the reaction. The yield of this product is consistently higher from the i-propanol than methanol photolysis, but the maximum yield, about 2%, is still some tenfold lower than that reported by Padwa and coworkers.⁹ The small variations in product yields with wavelengths of irradiation are within experimental error and probably no real trends are involved.

In triplet sensitization the solvent dependence is more marked: in methanol the rearranged products still predominate, but in i-propanol, acetophenone becomes the major product. The ester/acetophenone product ratios from these experiments are given in Table 10.

3.4.2 Non-polar solvents


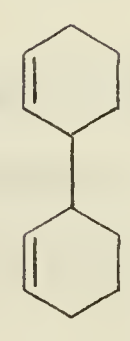
The direct photolysis of VI was also studied in cyclohexene using Pyrex filtered irradiation. The photosensitized decomposition of VI was examined using MK and a uranium glass filter. The results, presented in Table 11, are completely divergent from those reported in the literature:

- 1) there is a substantial difference in the yields of acetophenone in the direct and photosensitized decomposition. In the former case the yields are very small (viz. 70% claimed by Hammond et al)

Table 11

Product Yields from the Direct and Photosensitized

Photolysis of VI in Cyclohexene

Product	% Yield ^a									
	Direct ^b			Photosensitized ^c						
	1	2	3	1	2	3	4	5		
CO	3	2	2				2	2		
PhCOCH ₃	4	2	3	42	46	39	33	33		
	2	2	2				traces	traces		
Dilactone			~28				not measured			
							not measured	quantitatively		

a) Based on the amount of starting material used.

b) 10-15 mg/cc.

c) 5-7 mg/cc.

whereas in the latter case, as expected, acetophenone is the major product.

- 2) substantial amounts of dilactone were formed, which were underestimated by Hammond et al. Dilactone was formed as a solid suspension in the solution and after evaporation of the solvent, it was separated by adding diethyl ether. Creamy crystals (m.p. 285-286°) were collected and identified by comparing the m.p. and i.r. data reported by Yates et al.¹² The parent peak of the mass spectrum at m/e 235 corresponds to the monomer, P-1.

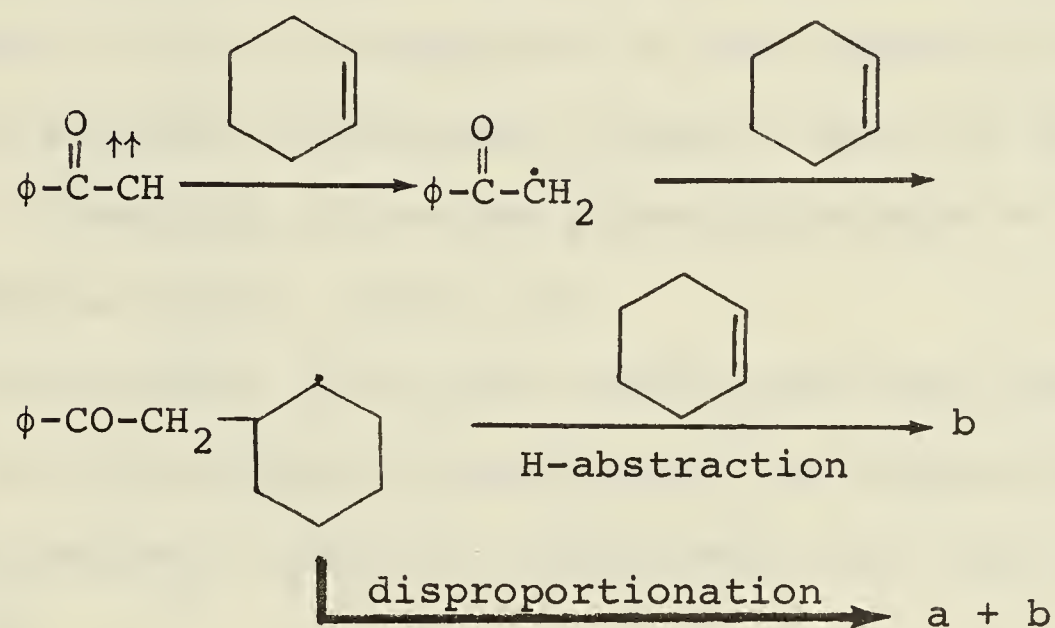
Other products formed in addition to those listed in Table 11 are:

- 1) Phenylacetic acid. It was formed in small and equal amounts in both the sensitized and unsensitized reactions and probably arises from the addition of phenylketene to traces of water in cyclohexene;
- 2) Trace amounts of a compound of empirical formula $C_{12}H_{18}O$ (MS 9): m.s. m/e 178 (parent); i.r. (CCl_4): 1700 cm^{-1} (C=O); n.m.r. (CCl_4): δ 1.4 - 2.6, m, 18 (H).
- 3) Two additional unidentified compounds:
 - a) m.s. m/e 200 (parent); i.r. (CCl_4): 1735 cm^{-1}

(C=O), 3035 cm^{-1} (-CH=).

b) m.s. m/e 202 (parent); i.r. (CCl_4): 1735 cm^{-1} (C=O).

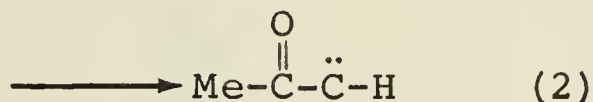
These could arise from the addition and/or insertion reaction of the ketocarbene with cyclohexene, followed by H-abstraction or disproportionation:



CHAPTER 4DISCUSSION

The results obtained under various conditions on the isotopic scrambling reactions in the diazopropanone system are summarized in Table 12. It is seen that scrambling in the diazoketone→ketene transformation is small, of the order of 3-7%, irrespective of the isomeric structure of the starting diazoketone, phase or mode of decomposition. Scrambling in the gas phase photolysis of methylketene is larger, about 16%.

It is clear from these results that the controlling step in the isotopic scrambling of the diazoketone→ketene rearrangement cannot be exclusively the ring opening process:



For if it were, one isomeric diazoketone should give low scrambling while the other should lead to extensive scrambling in the position of the ^{13}C labelling. The absence of scrambling is more likely due to the inefficiency

Table 12

Summary of Experimental Results

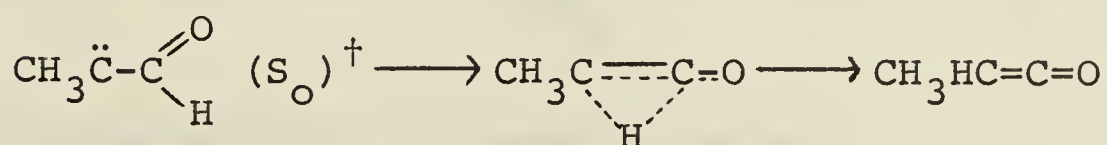
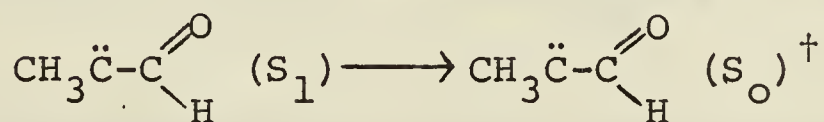
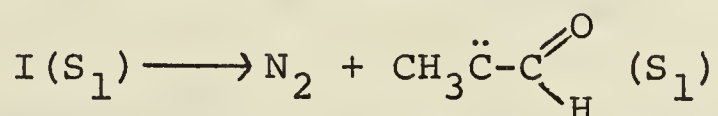
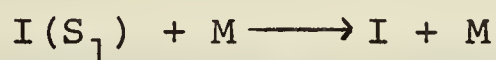
Compound	Phase	Reaction	% ^{13}C in CO	% ^{13}C in Me-propionate	% Scrambling
$^{13}\text{CO}^{\text{a}}$					
2-diazopropionaldehyde-	gas	photo	24.4	--	19.2
	CH_3OH	photo	--	28.7	5
	gas	thermal	--	29	5
$^{13}\text{CO}^{\text{b}}$					
α -diazacetone-	gas	photo	68.0	--	20.5
	CH_3OH	photo	--	80.7	6.7
	gas	thermal	--	80.4	6.9
Methylketene ^c	gas	photo	68.8	--	16

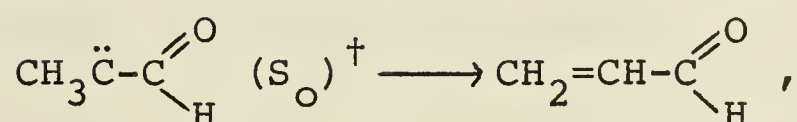
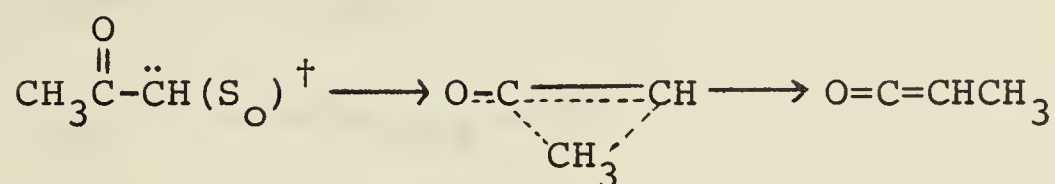
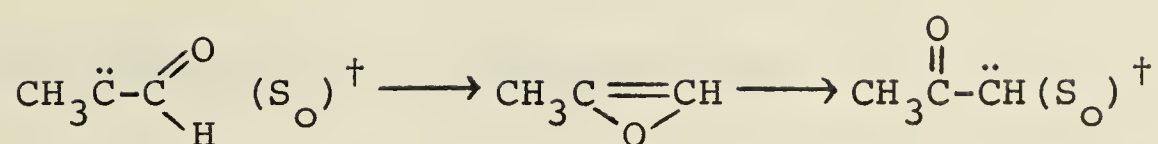
^a30.2% ^{13}C . ^b86.2% ^{13}C . ^c80.7% ^{13}C on C=O; 5.8% ^{13}C on -CH=.

of ring closure, the reverse of steps (1) and (2), and consequently to the absence of oxirene formation.

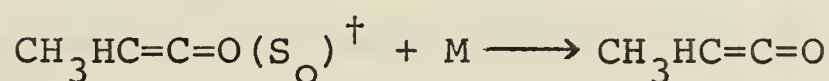
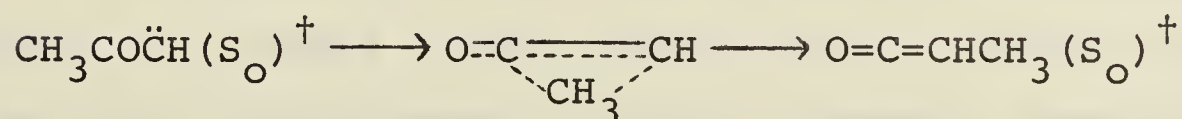
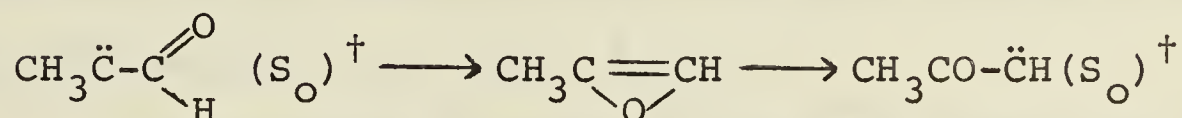
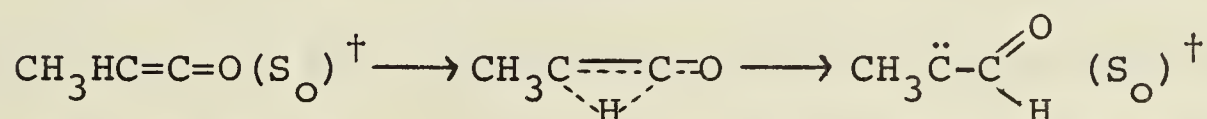
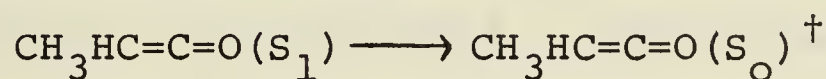
One may be tempted to generalize and to attribute the absence of scrambling in any diazoketone photolysis to the absence of oxirene formation. This, however, is not the case. From the analogous and parallel studies of Dr. B. Kim in this laboratory on the isomeric diazoketones $\phi\text{COCN}_2\text{CH}_3$ and $\text{CH}_3\text{COCN}_2\phi$, it would appear that in this case scrambling is largely determined by the mode of ring opening; $\text{CH}_3\text{COCN}_2\phi$ gave 12% scrambling while the other isomer gave 84%.

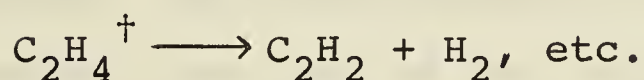
The mechanism of the gas phase photodecomposition of I can be delineated by the following sequence of elementary steps:





where M is a deactivator molecule, S_0 is the singlet ground state, S_1 is the lowest excited singlet state and the dagger signifies vibrational excitation. These processes are then followed by the polymerization and photolytic decomposition of methyl ketene:





The validity of this mechanism is based on the nature of the products and extensive theoretical studies using Extended Hückel Molecular Orbital (EHMO) theory for the calculation of orbital and state energies and orbital symmetry correlations.²²

A similar mechanism applies for the solution phase photolysis. In alcoholic solution however, the ketene is rapidly and nearly quantitatively scavenged, preventing its photolysis. Interestingly, the isotopic scrambling in the methyl propionate product, 5%, is approximately equal to the scrambling obtained in the gas phase photolysis after correction for scrambling in the methyl ketene photolysis, $19.2 - 16 = 3.2\%$.

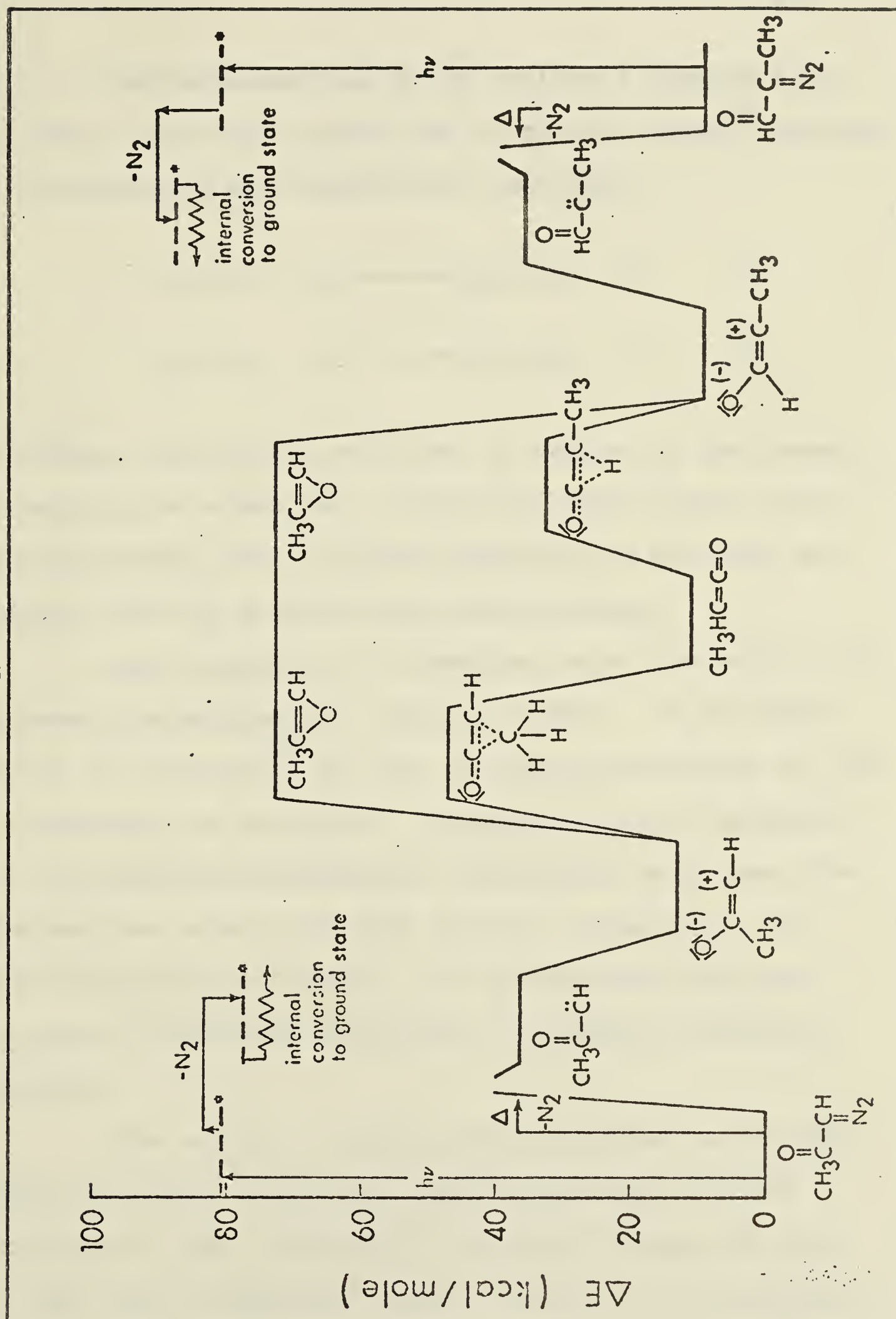
In previous studies it has been shown that the precursor of oxirene is the vibrationally excited ground singlet state ketocarbene. Orbital symmetry considerations require the ketocarbene from the photochemical decomposition of the diazoketone to be formed in the lowest

excited singlet state. Since oxirene formation is orbital symmetry allowed only from the ground state of the ketocarbene, a rapid internal conversion to yield a vibrationally excited ground state ketocarbene is invoked in the mechanism. EHMO calculations predict a high stability for the zwitter ion form of the various ketocarbenes studied, and it was proposed that isomerization to oxirene or ketene occurs by the appropriate geometrical changes in the zwitter ion. The enthalpy changes for the decomposition of α -diazopropanones, as obtained from EHMO calculations, are illustrated in Figure 6.²² From this it is seen that the oxirene state lies above the cyclic transition state for isomerization to ketene. The latter can be reached from the ground state of the ketocarbene, whereas only vibrationally excited ketocarbenes can attain the oxirene forming state. Photolytic production of the carbene provides sufficient excess vibrational energy but low temperature thermolysis produces the carbene in the ground electronic state without excess vibrational energy. Hence oxirene formation is a typical photo reaction.

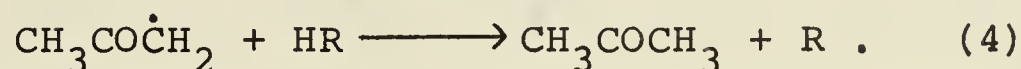
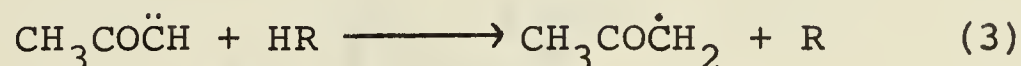
It is also relevant to mention that, according to EHMO calculations, oxirene and its simple methyl derivatives are inherently unstable with respect to C-O bond cleavage and they are predicted to exist only as short-lived transients.

Figure 6

Calculated enthalpy changes for the decomposition of 2-diazopropionaldehyde and α -diazoacetone.



The decomposition of IV follows a similar reaction path. The small quantities of acetone formed indicate the occurrence of the abstraction reactions



The carbene involved in reaction (3) may be in the lowest excited triplet state for, as will be shown below, triplet ketocarbenes have a higher aptitude for hydrogen abstraction than do singlet state ketocarbenes.

Small amounts of scrambling were observed in the gas phase thermolyses of I and IV at 180°. In the thermolysis of azibenzil⁴⁰ at 100° or ethyldiazoacetate at 140° no scrambling was detected. It appears that in agreement with the postulated mechanism, thermolysis at or near the decomposition points proceeds without scrambling. At higher temperatures, however, the ketocarbene acquires sufficient vibrational excitation to undergo scrambling reactions.

The extent of oxirene participation in the photolysis of methyl ketene was relatively small, of the same order as that observed for dimethyl ketene but smaller than that in diphenyl ketene. This is to be expected,

since deactivation and decomposition of the hot ketene molecule always compete with rearrangement. Consider the simple RRK formula for chemical activation:

$$k = A \left(\frac{E_T - E_a}{E_T} \right)^{s-1},$$

where E_T is the total energy available for reaction, E_a is the activation energy, "s" is the number of normal modes and k and A are the rate constant and pre-exponential factor, respectively. It can be readily shown that an increase in the value of "s" has a larger decelerating effect on the process having a larger activation energy. Thus, since $E_a(\text{decomp}) > E_a(\text{oxirene})$ and

$$\frac{k_d}{k_{\text{oxirene}}} = \frac{A_d}{A_{\text{oxirene}}} \left(\frac{E_T - E_a(\text{decomp})}{E_T - E_a(\text{oxirene})} \right)^{s-1},$$

an increase in "s" will decrease the ratio k_d/k_{oxirene} .

The present results on the photolysis and sensitized decomposition of α -diazacetophenone are summarized for convenience in Table 13 along with the literature data, and conclusively demonstrate that the reactive species in the Wolff rearrangement is a singlet. There is no obvious explanation for the discrepancy between the present results and those reported by Hammond and coworkers.

Table 13

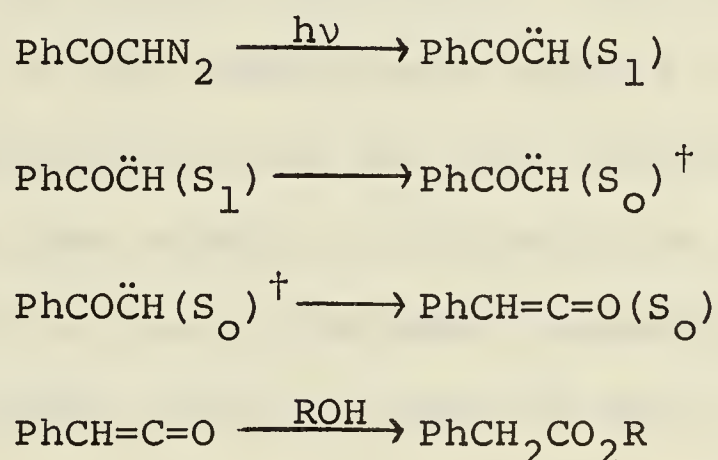
Direct and Sensitized Photolysis of α -Diazoacetophenone

Solvent	Yields, %				Reference
	PhCOCH ₃	PhCH ₂ COOR	Dilactone	7-norcaryl	Phenyl Ketone
cyclohexene	>70	-	trace	10-12	10
	>70 ^a	-	-	12	10
	3	-	28	2	this work
	36 ^a	-	not determined ^a	traces ^a	this work
MeOH	trace	85			this work
	10	64 ^a			this work
	trace	63			9
	12 ^{a,b}	88 ^{a,b}			9
i-PrOH	2	72			this work
	50 ^a	2 ^a			this work
	23	57			9
	>99 ^{a,b}	<1 ^{a,b}			9

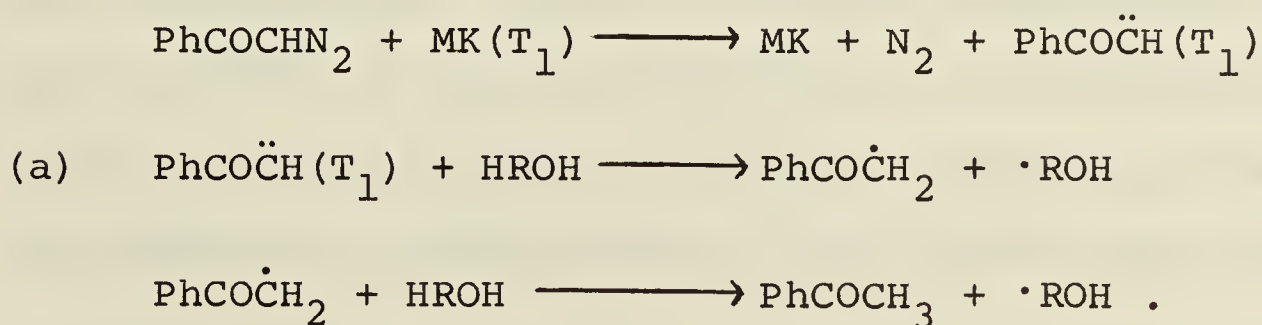
^aSensitized with Michler's ketone.^bRelative yields calculated from the product ratios.

kers and Padwa and coworkers. Since in the present study great care was taken in product identification and measurement and the results are in agreement with the known reactions of singlet and triplet state ketocarbenes, it is believed that the earlier literature data are in error.

The direct photolysis of diazoacetophenone in hydroxylic solvents leads to high yields of the rearranged product, phenylacetic acid ester:



whereas in triplet Michler's ketone sensitization the major retrievable product is acetophenone, the hydrogen abstraction product of the triplet ketocarbene:



Hydrogen abstraction however, competes with collisional

relaxation to the ground state:

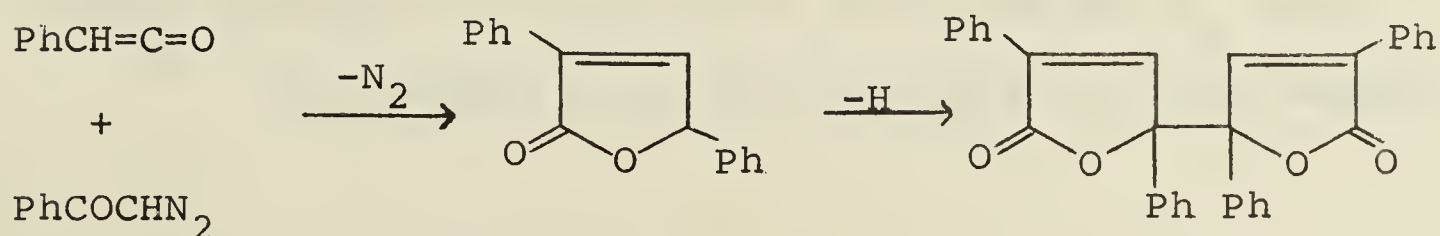


If hydrogen abstraction becomes more difficult due to an increase in the CH bond strength of the donor molecule, the ratio of the rate constants, k_a/k_b , will decrease. This was indeed observed in going from isopropanol to methanol solution.

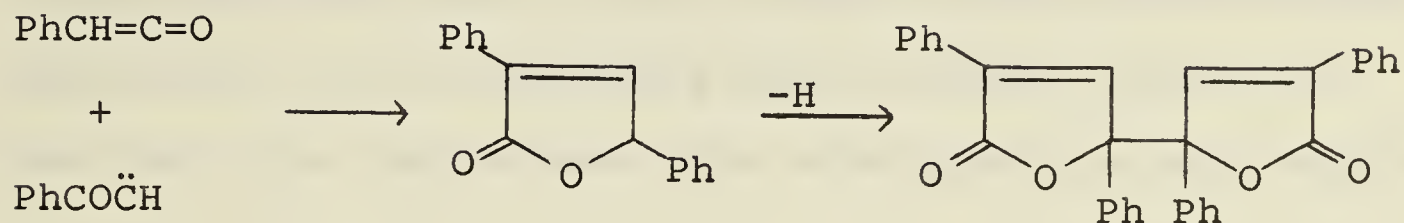
In the direct photolysis, the intervention of the triplet state of the ketocarbene appears to be insignificant, as manifested by the low rate constant ratios k_a/k_b . The mechanism most readily envisioned for singlet carbene transformation is the collisional relaxation of the initially formed higher lying S_1 state to the T_1 level:



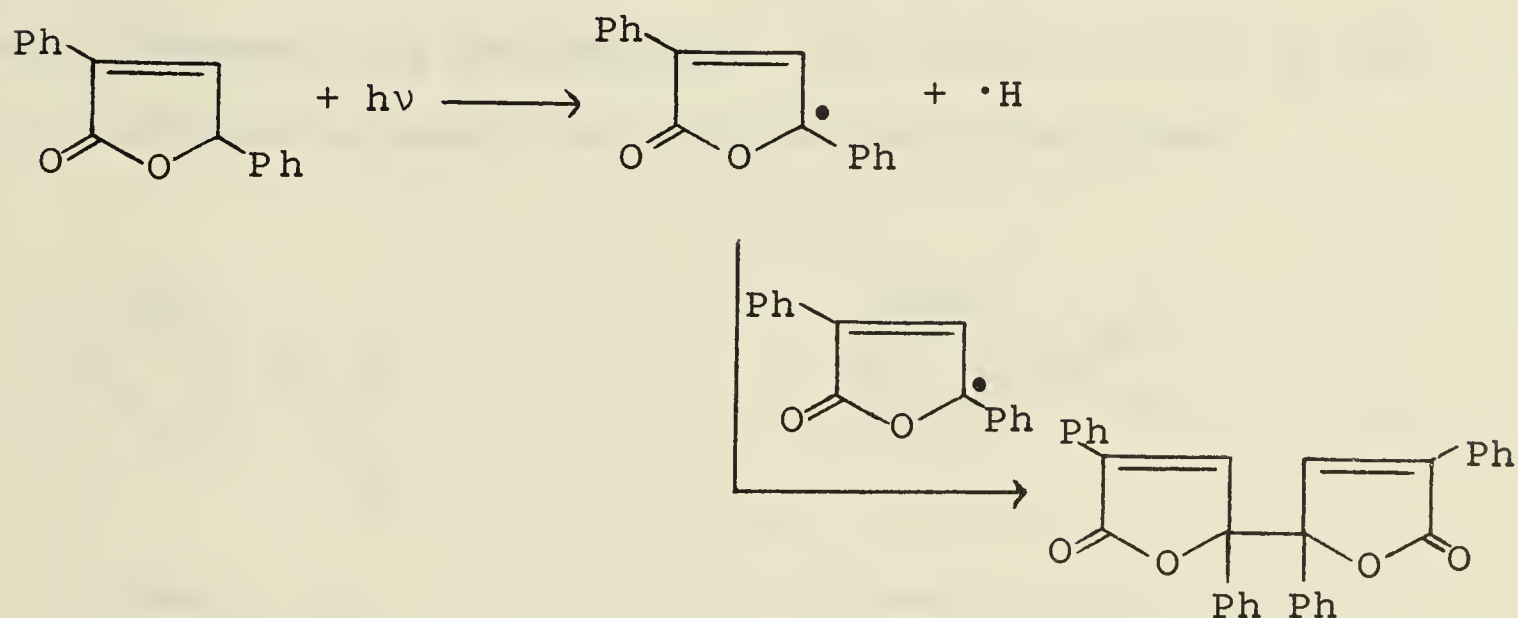
The decomposition in cyclohexene can also be rationalized in terms of singlet and triplet state carbene intervention. Thus, in triplet sensitization the major product is again acetophenone. In the direct photolysis the major product, dilactone, presumably forms via the addition of phenylketene to the parent diazo molecule;



or via addition of the ketocarbene to phenyl ketene:



Dimerization of the lactone is probably a photo-initiated process:



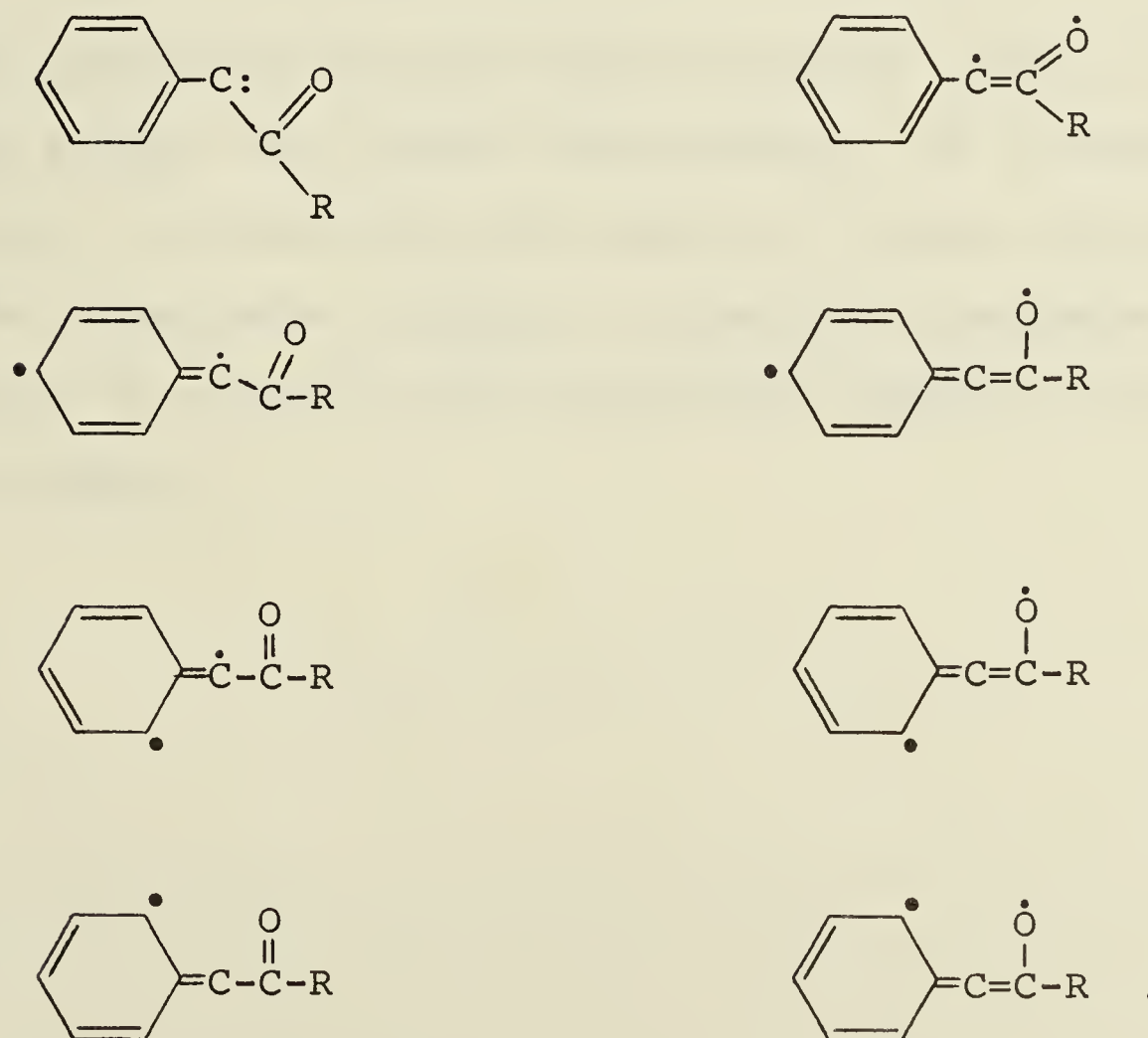
Thus, it is now possible to explain the high yield of scrambling, 57%, observed in the triplet Michler's ketone sensitized photolysis of $\text{Ph}\overset{*}{\text{C}}\text{OCN}_2\text{H}$ in cyclopentane solution.⁴⁰ Owing to the slow rate of hydrogen abstraction the triplet ketocarbene undergoes intersystem crossing to the ground state S_0 having only slightly less excess vibrational energy than that from the S_1 state.

At present it is not possible to fully explain

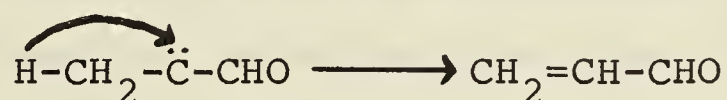
the observed trends in the efficiency of the isotopic scrambling reactions of the various diazoketones studied. Nonetheless, it is suggested that a phenyl group in a position α to the carbene site stabilizes the ketocarbene



and preferential ring opening in the oxirene structure would become rate determining. The stabilization is due to resonance between the contributing structures:



The yields of abstraction products derived from triplet state ketocarbenes in the photolyses of α -diazoacetone and 2-diazopropionaldehyde are also very small, less than 2%. In the case of α -diazoacetone only negligible amounts of acetone ($\sim 0.6\%$) were formed. Acrolein, from the photolysis of 2-diazopropionaldehyde, was found in slightly higher amounts (2.2%) but its mode of formation is not certain. It probably arises from an H-atom shift in the ketocarbene.

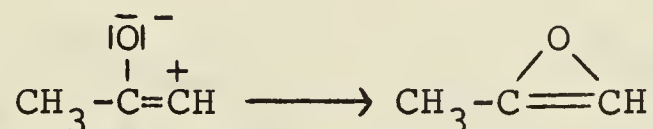


but since this process would be equally feasible in both the singlet and triplet ketocarbenes, the acrolein yields cannot be identified with those of triplet ketocarbene. The accumulative evidence is therefore overwhelming and there is no doubt that the reactive species in the WR is a singlet.

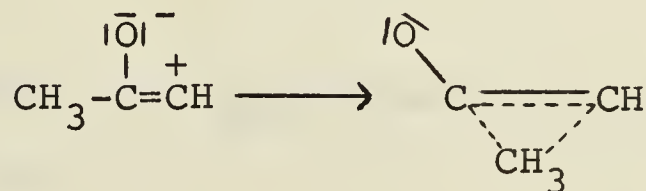
CHAPTER 5

SUMMARY AND CONCLUSIONS

The gas phase photolyses of the asymmetrically substituted diazoketones $\text{CH}_3^*\text{COCHN}_2$ and $\text{CH}_3\text{CN}_2^*\text{CHO}$ showed that ~20% scrambling had occurred in the transformation. The intermediacy of oxirene now appears to be a characteristic feature of the photochemical WR of α -diazoketones. By using this isomeric pair of substrates, it was hoped that some information regarding the rate controlling step might be derived, in particular, what effect the H or CH_3 substituent might have on the relative rate of ring closure, e.g.



and group migration:

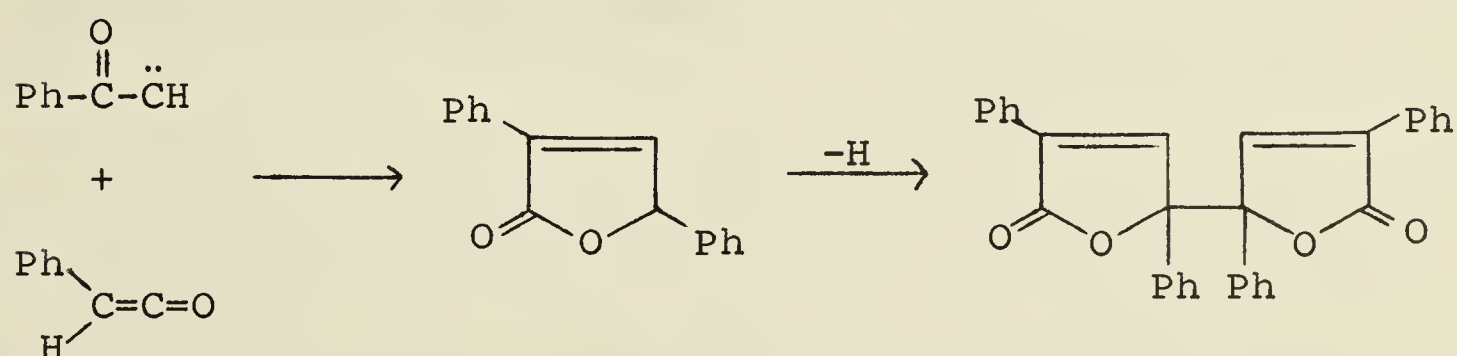


Since the degree of scrambling was very small and almost identical in the two cases, it appears that H and CH_3 migration in the ketene-forming step is faster than ring closure and that oxirene is a relatively minor intermedi-

ate in the WR of diazopropanones.

Scavenging of methylketene by methanol in the liquid phase led to the formation of the ester in which the labelling was only 6% scrambled. This is in agreement with the scrambling found in the photolysis of methylketene, 16% indicating that most of the scrambling in the WR occurs in the secondary photolysis of the primary ketene product.

The direct photolysis and triplet sensitization of α -diazacetophenone yielded product ratios which were significantly different from those reported in the literature. The direct photolysis in cyclohexene yielded dilactone,

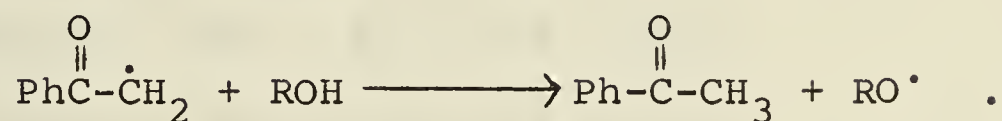
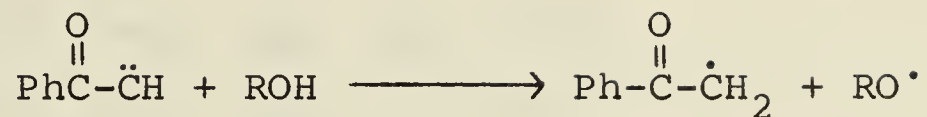


whereas in methanol and isopropanol the major products are esters formed via



Triplet photosensitization with Michler's Ketone however,

yielded mainly acetophenone:



The acetophenone yields increased with decreasing C-H bond strength in the alcohol as expected in an abstraction reaction.

The high yields of the rearranged product obtained in direct photolysis conclusively prove that the reactive intermediate in the photochemical WR of α -diazo-ketones is a singlet and that previous literature claims to the contrary are in error.

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B30049